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[54] SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

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[57] ABSTRACT

A silver halide photographic light-sensitive material comprising a support having thereon a photographic silver halide emulsion layer containing a magenta coupler, a photographic silver halide emulsion layer containing a yellow coupler, a photographic silver halide emulsion layer containing a cyan coupler and an non-light-sensitive layer containing a binder and a UV absorbent, wherein said silver halide photographic light-sensitive material has not more than 7.6 g/m² of gelatin, said UV absorbent is liquid at an ordinary temperature, and said magenta coupler is a compound represented by Formula I;

Formula I

wherein Z represents a non-metallic group necessary to form a nitrogen-containing heterocyclic ring, X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent, and R represents a hydrogen atom or a substituent.

20 Claims, No Drawings

SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

This invention relates to a silver halide photographic light-sensitive material and, more particularly, to a silver halide photographic light-sensitive material improved in image quality and physical properties.

BACKGROUND OF THE INVENTION

Generally, a silver halide photographic light-sensitive material is coated thereon with silver halide emulsion layers so spectrally sensitized as to have desired light sensitivities, respectively, so that a dye image can be formed upon reaction of a color developing agent with each of the yellow, magenta and cyan dye-forming couplers contained in the silver halide emulsion layers, respectively.

Among these couplers, the 5-pyrazolone type couplers having so far been used as magenta dye-forming couplers have a serious problem of a yellow stain causing a non-color-developed portion a yellowish color change when applying heat or temperature to them, 25 that is so-called Y-stain, because the formed dyes have a side- absorption around 430 nm that is undesirable for color reproduction.

There are magenta couplers such as those of pyrazolobenzimidazole described in, for example, British Patent No. 1,047,612, those of indazoles described in, for example, U.S. Pat. No. 3,770,447, and those of pyrazoloazoles described in, for example, U.S. Pat. No. 3,725,067, British Patent Nos. 1,252,418 and 1,334,515, Japanese Patent Publication Open to Public Inspection -hereinafter referred to as Japanese Patent O.P.I. Publication- Nos. 59-162548/1984 and 59-171956/1984. The dyes formed of the above-given magenta couplers have an extremely small side-absorption around 430 nm and extremely few Y-stains produced by heat or temperatures.

However, the dyes formed of the above-mentioned pyrazoloazole type couplers are low in light-fastness and, particularly, the commercial values thereof are seriously spoiled when they are used for color papers for direct appreciation. Therefore, various improvements thereof have been studied to solve the problems.

As for one of the improvements, there are some proposals for using various kinds of antifading agents and UV absorbents in combination. To obtain a satisfactory effect, a large amount thereof should be used. Resultingly, oil drops are increased to very often produce a sweating phenomenon, that is a phenomenon that the oil drops contained in a light-sensitive material are diffused and flocculated to produce liquid drops on the surface of the light-sensitive material or to make the liquid drops adhere to the surface thereof when the light-sensitive material is stored under the high temperature and high humidity conditions.

To inhibit the light-sensitive material from producing a sweating phenomenon, it is effective to increase an amount of binders to be added. However, it is found that only a simple increase of a gelatin content is not any decisive means at all for solving the problem, but a 65 cause of the deteriorations of the white-background property and color reproducibility of the processed light-sensitive material. The simple increase thereof also

produces, particularly. Y-stains, though the sweating phenomenon may be reduced to some extent.

On the other hand, silver halide emulsions having a high silver chloride content have preferably been used to meet the recent rapid-processing requirements. It is, however, found that some kind of highly silver chloride containing grains produce a desensitization caused by a physical pressure, and that the deteriorations are amplified in an emulsion containing the above-mentioned magenta couplers, though a rapid processing speed may be provided.

As for the means for improving the above-described pressure- desensitization and pressure-fog production, some methods have been known, in which any pressure does not affect silver halide grains, that is to say, the methods in which various gelatin, polymers and organic compounds are used in protective layers, interlayers or silver halide-containing layers.

There may be, for example, the combination use of the heterocyclic compounds given in British Patent No. 738,618, alkyl phthalates given in British Patent No. 738,637, alkyl esters given in British Patent No. 738,639, hydrophilic compounds including, particularly, polyhydric alcohol given in U.S. Pat. No. 2,960,404, carboxyalkyl cellulose given in U.S. Pat. No. 3,121,060, paraffin and carboxylates given in Japanese Patent 0.P.I. Publication No. 49-5017/1974, glycerol derivatives and ether or thioether compounds given in Japanese Patent O.P.I. Publication No. 51-141623/1976, organic high boiling compounds not miscible with any hydrophilic binders given in Japanese Patent 0.P.I. Publication No. 53-85421/1978, alkyl acrylates and organic acids given Japanese Patent Examined Publication No. 53-28086/1978, and liquid type UV absorbents and vinyl sulfon type hardeners given in Japanese Patent O.P.I. Publication No. 63-46439/1988.

In the above-described methods, the improvement effects of pressure-desensitization are not yet satisfactory, so that there are demands for a light-sensitive material high in resistance against pressure-sensitization and pressure-desensitization which may be derived from the increase in the transport speed of an automatic processor introduced to meet the wide application of rapid processes.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a silver halide photographic light-sensitive material capable of solving the above-described problems.

Another object of the invention is to provide a silver halide photographic light-sensitive material capable of giving an excellent image quality and showing excellent physical properties even under various conditions.

DETAILED DESCRIPTION OF THE INVENTION

The above-mentioned objects of the invention can be achieved with a silver halide photographic light-sensitive material comprising a support having thereon a photographic silver halide emulsion layer containing a magenta coupler, a photographic silver halide emulsion layer containing a yellow coupler, a photographic silver halide emulsion layer containing a cyan coupler and an non-light-sensitive layer containing a binder and a UV absorbent, wherein said silver halide photographic light sensitive material has not more than 7.6 g/m² of gelatin, said UV absorbent is liquid at an ordinary temperature,

and said magenta coupler is a compound represented by Formula I;

wherein Z represents a non-metalic group necessary to form a nitrogen-containing heterocyclic ring, provided, the rings formed by Z may each have a substituent;

X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a 15 color developing agent; and

R represents a hydrogen atom or a substituent. Now, the invention will be further detailed.

In the magenta couplers represented by Formula I, there is no special limitation to the substituents represented by R. However, they include, typically, each of the groups of alkyl, aryl, anilino, acylamino, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl and, besides, halogen atoms and each of the groups of cycloalkenyl, alkinyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, 25 acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic-oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxycarbonyl, aryloxycarbonyl and heterocyclic-thio; spirocompound residual groups; and cross-linking hydrocarbon compound residual groups.

As for the alkyl groups represented by R, those having 1 to 32 carbon atoms are preferably used and they may be either straight-chained or branched.

As for the aryl groups represented by R, a phenyl group is preferably used.

The acylamino groups represented by R include, for example, an alkylcarbonylamino group and an arylcarbonylamino group.

The sulfonamido groups represented by R include, for example, an alkylsulfonylamino group and an arylsulfonylamino group.

In the alkylthio and arylthio groups each represented by r, the alkyl and aryl components thereof include, for example, the foregoing alkyl and aryl groups each represented by R.

As for the alkenyl groups represented by R, those having 2 to 32 carbon atoms are preferably used and, as 50 for the cycloalkyl groups represented by R, those having 3 to 12 carbon atoms and, particularly, 5 to 7 carbon atoms are preferably used; provided, the alkenyl groups may be either straight-chained or branched.

As for the cycloalkenyl groups represented by R, 55 those having 3 to 12 carbon atoms and, particularly, 5 to 7 carbon atoms are preferably used.

The sulfonyl groups represented by R include, for example, an alkylsulfonyl group and an arylsulfonyl group;

The sulfinyl groups include, for example, an alkylsulfinyl group and an arylsulfinyl group;

The phosphonyl groups include, for example, an alkylphosphonyl group, an alkoxyphosphonyl group, an aryloxyphosphonyl group, and an arylphosphonyl 65 group;

The acyl groups include, for example, an alkylcarbonyl group and an arylcarbonyl group; The carbamoyl groups include, for example, an alkylcarbamoyl group and an arylcarbamoyl group:

The sulfamoyl groups include, for example, an alkyl-sulfamoyl group and arylsulfamoyl group;

The acyloxy groups include, for example, an alkylcarbonyloxy group and an arylcarbonyloxy group;

The carbamoyloxy groups include, for example, an alkylcarbamoyloxy group and an arylcarbamoyloxy group;

The ureido groups include, for example, an alkylureido group and an arylureido group;

The sulfamoylamino groups include, for example, an alkylsulfamoylamino group and an arylsulfamoylamino group;

As for the heterocyclic groups, those having 5 to 7 carbon atoms are preferably used. They include, typically, a 2-furyl group, a 2-thienyl group, a 2-pyrimidinyl group and a 2-benzothiazolyl group;

As for the heterocyclic-oxy groups, those having a 5to 7-membered ring are preferably used. They include, for example, a 3,4,5,6-tetrahydropyranyl-2-oxy group and a 1-phenyltetrazole-5-oxy group;

As for the heterocyclic-thio groups, those having a 5to 7-membered ring are preferably used. They include, for example, a 2-pyridylthio group, a 2-benzothiazolylthio group and a 2,4-diphenoxy-1,3,5-triazole-6-thio group;

The siloxy groups include, for example, a trimethyl-siloxy group, a triethylsiloxy group and a dimethyl-butylsiloxy group;

The imido groups include, for example, a succinimido group, a 3-heptadecylsuccinimido group, a phthalimido group and a glutarimido group;

The spiro-compound residual groups include, for example, a spiro [3.3]heptane-1-yl group;

The cross-linking hydrocarbon compound residual groups include, for example, a bicyclo [2.2.1] heptane-1-yl, tricyclo [3.3.1.1^{3.7}] decane-1-yl, and 7,7-dimethyl-bicyclo [2.2.1] heptane-1-yl;

The groups capable of being split off upon reaction with the oxidized products of a color developing agent include, for example, halogen atoms such as a chlorine, bromine and fluorine atom, and each group of alkoxy, aryloxy, heterocyclic-oxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl, alkyloxalyloxy, alkoxyoxalyloxy, alkylthio, arylthio, heterocyclic-thio, alkyloxythiocarbonylthio, acylamino, sulfonamido, nitrogen-containing heterocyclic ring bonded with an N atom, alkyloxycarbonylamino, aryloxycarbonylamino, carboxyl, and

$$R_{2}'-C-R_{3}'$$
 R_{1}'
 $N-N$

wherein R₁ is synonymous with the foregoing R; Z' is synonymous with the foregoing Z; and R₂ and R₃ represent each a hydrogen atom, an aryl group, an alkyl group, or a heterocyclic group. Among them, a halogen atom and, particularly, chlorine atom may preferably be used.

The nitrogen-containing heterocyclic rings each formed with Z or Z' include, for example, a pyrazole ring, an imidazole ring, a triazole ring and a tetrazole

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ring, and the substituents of the foregoing rings include those given by the foregoing R.

Those represented by Formula I can further be represented typically by the following formulas II through VII:

$$R_1$$
 N
 N
 N
 R_2

$$\begin{array}{c|c}
X & H \\
N & N
\end{array}$$

$$\begin{array}{c|c}
R_1 & & \\
N & & N
\end{array}$$

$$R_1$$
 N
 N
 N
 N
 N
 N
 N
 N
 N

$$\begin{array}{c|c}
R_1 & H \\
\hline
N & N
\end{array}$$

$$\begin{array}{c|c}
R_1 \\
\hline
N & R_2
\end{array}$$

$$R_1$$
 R_7
 R_7

$$\begin{array}{c|c}
X & H \\
N & N
\end{array}$$

Formula II

Formula III

Formula V

Formula VII

The preferable among those represented by Formula I are represented by Formula VIII given below:

$$\begin{array}{c|c}
X & H \\
N & N \\
N & N
\end{array}$$

wherein R_1 , X and Z_1 are each synonymous with R, X and Z each denoted in Formula I.

Among the magenta couplers represented by Formulas II through VII. the particularly preferable are those 5 represented by Formula II.

The most preferable substituents represented by R and R₁ on the foregoing heterocyclic rings are those represented by Formula IX given below:

$$R_{10}$$
 R_{10}
 R_{10}
 R_{11}
Formula IX

15 wherein R₉, R₁₀ and R₁₁ are synonymous with those represented by the foregoing R.

Any two of the above-denoted R9, R10 and R11, for example, R9 and R10, are allowed to form a saturated or unsaturated ring such as cycloalkane, cycloalkene and 20 heterocyclic rings, upon coupling of R9 to R10. It is also allowed to constitute a cross-linking hydrocarbon compound residual group upon coupling of R11 to the ring.

In Formula IX, it is preferable that (i) at least two of R9 through R11 are alkyl groups and (ii) One of R9 25 through R₁₁, R₁₁ for example, is a hydrogen atom and the other two, R₉ and R₁₀ for example, are coupled together to form a cycloalkyl group with a root carbon atom.

It is further preferable for the above-given case (i) 30 that two of R₉ through R₁₁ are alkyl groups and one of the rest is a hydrogen atom or an alkyl group. In the rings formed with Z denoted in Formula I and the rings formed with Z1 denoted in Formula VIII. The substituents which the rings may have, and R2 through R8 35 denoted in Formulas II through VI, are preferably represented by the following Formula X:

$$-R^1$$
-SO₂- R^2 Formula X

wherein R¹ represents an alkylene group, and R² represents an alkyl, cycloalkyl or aryl group.

The alkylene groups represented by R1 are preferable to have not less than two carbon atoms and, more preferably, 3 to 6 carbon atoms in the straight-chained por-Formula VIII 45 tion thereof, and they are regardless of the straightchained and the branched.

The cycloalkyl groups represented by R² include preferably those each having 5- or 6-membered ring.

The typical examples of the compounds relating to the invention will be given below:

$$\begin{array}{c|c} CI & H \\ N & N \\ \hline N & M \\ \hline N & CHCH_2SO_2C_{18}H_{37} \\ \hline CH_3 & CHCH_2SO_2C_{18}H_{37} \\ \hline \end{array}$$

$$CH_3 \xrightarrow{N} N \xrightarrow{N} CH_3 \xrightarrow{N} CH_2SO_2C_{18}H_{37}$$

$$CH_3$$

$$C_{12}H_{25}O$$
 SO_2NH
 $C_{12}H_{25}O$
 N
 N
 N
 $C_4H_9(t)$

CH₃

$$N$$
 N
 CH_3
 CH_3

$$\begin{array}{c|c} Cl & H & OC_8H_{17} \\ \hline N & N & OC_8H_{17} \\ \hline CHCH_2NHSO_2 & OC_8H_{17} \\ \hline CH_3 & NHSO_2 & C_8H_{17}(t) \end{array}$$

(i)
$$C_3H_7$$
N
OC₄H₉

$$N$$
 $C_8H_{17}(t)$

$$\begin{array}{c|c} NHSO_2CF_3 & I-13 \\ \hline \\ H & N \\ \hline \\ N & N \\ \hline \\ N & CH_2CH_2SO_2 \\ \hline \\ \end{array} \begin{array}{c} NHSO_2C_{16}H_{33} \\ \hline \end{array}$$

I-16
$$COOH$$

$$H$$

$$N$$

$$N$$

$$CO$$

$$C_{18}H_{35}$$

$$CO$$

$$C_{18}H_{35}$$

$$\begin{array}{c|c} & Br & H & C_5H_{11}(t) \\ \hline N & N & C_5H_{11}(t) \\ \hline N & C_6H_{13} & C_5H_{11}(t) \end{array}$$

(i)
$$C_3H_7$$
N
N
(CH₂)₂
NHCOCHO
C₅H₁₁(t)
C₅H₁₁(t)

$$C_4H_9$$
 C_1
 C_2H_5
 C_1
 C_1
 C_1
 C_2H_5
 C_1
 C_1
 C_2H_1
 C_1
 C_1
 C_2H_1
 C_1
 C_2H_1
 C_1
 C_2H_1
 C_1
 C_2H_1
 C_2H_1
 C_1
 C_2H_1
 C

$$\begin{array}{c|c} H & OC_4H_9 \\ \hline N & N & OC_4H_9 \\ \hline N & N & C_8H_{17}(t) \end{array}$$

(t)C₄H₉

$$\begin{array}{c}
C_1 \\
N \\
N
\end{array}$$
CHCH₂CH₂SO₂C₁₆H₃₃

$$CH_3$$

(1)C₄H₉

$$\begin{array}{c|c}
Cl & H \\
N & CH_3 \\
\hline
C & CH_2SO_2
\end{array}$$

$$\begin{array}{c|c}
CC_{12}H_{25}
\end{array}$$

$$(t)C_4H_9 \longrightarrow \begin{pmatrix} C_1 & H & \\ &$$

$$(t)C_4H_9 \longrightarrow N \longrightarrow N \longrightarrow CH_3 \longrightarrow CH_2CH_2C-NHCOCHO \longrightarrow NHSO_2N(CH_3)_2$$

$$CH_3 \longrightarrow CH_2H_{25} \longrightarrow NHSO_2N(CH_3)_2$$

CI
$$NH$$

$$N$$

$$N$$

$$CHCH2SO2$$

$$CH3$$

$$NHCOCHCH2SO2C12H25$$

$$CH3$$

CONH N N (CH₂)₂
$$O(CH2)2OC12H25 $O(CH2)2OC12H25$ $O(CH2)2OC12H25 $O(CH3)$$$$

CH₃O
$$N$$
 N
 CH_3
 CH_3

$$C_{2}H_{5}S$$

$$N$$

$$N$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

$$C_{5}H_{11}(t)$$

(CH₃)₃CCH₂

$$N \longrightarrow N$$

$$N \longrightarrow N$$

$$(CH2)3SO2
$$OC_8H_{17}$$

$$OC_8H_{17}$$$$

CI
$$CH_2$$

$$N$$

$$N$$

$$N$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$NHSO_2C_{16}H_{33}$$

CI H OCH₂CON(C₂H₅)₂

$$N \longrightarrow N \longrightarrow CH_2CH_2SO_2 \longrightarrow C_8H_{17}(t)$$

$$CH_3 \xrightarrow{Cl} H \xrightarrow{N \longrightarrow N} CHCH_2SO_2 \xrightarrow{CHCH_2SO_2} OC_{12}H_{25}$$

$$CH_3 \longrightarrow N \longrightarrow N$$

$$CHCH_2NHSO_2 \longrightarrow OC_8H_{17}$$

$$CHCH_2NHSO_2 \longrightarrow OC_8H_{17}$$

$$NHSO_2 \longrightarrow C_8H_{17}(t)$$

$$O \longrightarrow C_4H_9(t)$$

$$O \longrightarrow C_{12}H_{25}$$

 $C_8H_{17}(t)$

-continued OC₈H₁₇ I-50 OC_4H_9 OC_4H_9

Cl Cl Cl
$$N = N = N$$
 $(CH_2)_3O = N = N = N$ $(CH_2)_3O = N$ $(CH_2)_$

(t)C₄H₉

$$N \longrightarrow N \longrightarrow N$$

CH₃
 CH_3
 $CH_2CH_2C-NHSO_2$
 CH_3
 CH_3

(t)C₄H₉

$$N \longrightarrow N \longrightarrow N$$

(t)C₄H₉

$$C_1$$
 C_1
 C_2
 C_3
 $C_{10}H_{21}$
 $C_5H_{11}(t)$

Cl
$$(CH_2)_3$$
 $OC_{12}H_{25}$ N N N N N

$$C_{15}H_{31}$$

x:y = 50:50

x:y = 50:50

$$CH_3 \xrightarrow{C1} \overset{H}{\overset{N}{\overset{N}{\longrightarrow}}} CHCH_2NHSO_2 \xrightarrow{C_8H_{17}(t)} C_8H_{17}(t)$$

Besides the above-given typical examples of the compounds relating to the invention, the additional examples of the compounds relating to the invention include the compounds denoted by Nos. $1 \sim 4$, 6, $8 \sim 17$, $19 \sim 24$, $26 \sim 43$, $45 \sim 59$, $61 \sim 104$, $106 \sim 121$, $123 \sim 162$ and $164 \sim 223$ out of the compounds given in the right upper column on page 18 to the right upper column on page 45 32 of Japanese Patent O.P.I. Publication No. 62-166339/1987.

The above-mentioned couplers can be synthesized with reference to the descriptions in Journal of the Chemical Society, Perkin I, 2047~2052, 1977,; U.S. 50 Pat. No. 3,725,067; and japanese Patent O.P.I. Publication Nos. 59-99437/1984, 58-42045/1983, 59-162548/1984, 59-171956/1984, 60-33552/1985, 60-43659/1985, 60-172982/1985 and 60-190779/1985.

The magenta couplers of the invention may be used in 55 an amount within the range of, normally, 1×10^{-3} to 1 mol per mol of silver halide and, preferably, 1×10^{-2} to 8×10^{-1} mol.

The magenta couplers of the invention can be used with the other kinds of magenta couplers in combina- 60 tion.

Next, Uv absorbents applicable to the invention which is liquid at an ordinary temperature -hereinafter referred to the liquid UV absorbents of the invention-will be detailed.

In the invention, the expression, "liquid at an ordinary temperature", means that, as defined in 'Dictionary of Chemistry' Kyoritsu Press, 1963 Ed., a UV

absorbent is so amorphous as to be fluidized at 25.C and has an approximately constant volume. Therefore, the melting point thereof shall not be limitative, as far as the UV absorbents have the above-mentioned characteristics. Such compounds are, however, to have a melting point of -100° to 30° C. and, preferably, 100° to 15° C.

The liquid UV absorbents of the invention may be each either a single compound or the mixtures thereof. As for the mixtures thereof, those comprising the group consisting of structural isomers may preferably be used. Such structural isomers are detailed in, for example, U.S. Pat. No. 4,587,346.

The liquid UV absorbents of the invention can take any structures, provided, they can satisfy the above-described requirements. However, from the viewpoint of the light fastness of their own, a 2-(2'-hydroxyphenyl) benzotriazole type compound represented by Formula a may preferably be used.

$$R_3$$
 Formula a R_1 R_1 R_2

wherein R₁, R₂ and R₃ represent each a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alk-

oxy group, an aryloxy group, an alkenyl group, a nitro group or a hydroxyl group.

The halogen atoms represented by R₁, R₂ and R₃ include, for example, a fluorine atom, a Chlorine atom. or a bromine atom.

As for the alkyl and alkoxy groups represented each by R_1 , R_2 and R_3 , those having $1 \sim 30$ carbon atoms may preferably be used and, as the alkenyl groups, those having $2 \sim 30$ carbon atoms may preferably be used. branched.

The above-given alkyl, alkenyl and alkoxy groups may further have substituents.

groups should preferably be an alkyl group and, more preferably, at least two of the groups should be alkyl groups.

The alkyl groups represented by R₁, R₂ and R₃ may 5 be any ones of the alkyl groups. However, at least one of them may preferably be either a tertiary or secondary alkyl group.

It is particularly preferable that the groups represented by R₁ and R₂ are alkyl groups and at least one of These groups may be either straight-chained or 10 the alkyl groups is either a tertiary or secondary alkyl group.

> The typical examples of the liquid UV absorbents of the invention will be given below:

$$R_3$$
 N
 N
 N
 R_1
 R_2

Exemplified compound No.	R ₁	R ₂	R ₃
UV-1L	- СН ₃	-C ₄ H ₉ (sec)	- Н
UV-2L	$-C_4H_9(sec)$	$-C_4H_9(t)$	$-C_4H_9(t)$
UV-3L	$-C_4H_9(sec)$	$-C_4H_9(t)$	C_4H_9
UV-4L	$-C_4H_9(sec)$	$-C_4H_9(t)$	$-C_5H_{11}(t)$
UV-5L	$-C_4H_9(sec)$	$-C_4H_9(t)$	$-C_5H_{11}$
UV-6L	$-C_4H_9(sec)$	$-C_5H_{11}(t)$	$-C_4H_9(t)$
UV-7L	$-C_4H_9(sec)$	$-C_5H_{11}(t)$	$-C_4H_9$
UV-8L	$-C_4H_9(t)$	$-C_4H_9(t)$	$-C_4H_9(sec)$
UV-9L	$-C_5H_{11}(t)$	$-C_5H_{11}(t)$	$-C_4H_9(sec)$
UV-10L	$-C_4H_9(t)$	$-C_5H_{11}(t)$	$-C_4H_9(sec)$
UV-11L	$-C_4H_9(sec)$	$-C_4H_9(sec)$	$-C_4H_9(t)$
UV-12L	$-C_4H_9(sec)$	$-C_4H_9(sec)$	$-C_4H_9$
UV-13L	$-C_4H_9(t)$	$-C_2H_4COOC_8H_{17}$	- H
UV-14L	-C ₄ H ₉ (1)	-C ₂ H ₄ COOCH ₂ CHC ₄ H ₉	—H
UV-15L	$-C_4H_9(t)$	-(CH ₂) ₂ COO(CH ₂) ₂ OC ₄ H ₉	—н
UV-16L	$-C_8H_{17}$	$-CH_3$	— н
UV-17L	$-c_{10}H_{21}$	$-CH_3$	— H
UV-18L	$-C_{12}H_{25}$	$-CH_3$	—H
UV-19L	$-C_{16}H_{33}$	$-CH_3$	— <u>H</u>
UV-20L	$-C_{20}H_{41}$	$-CH_3$	— Н
UV-21L	$-C_{22}H_{45}$	$-CH_3$	H
UV-22L	$-C_{24}H_{49}$	CH ₃	— H

The typical examples of the alkyl, alkenyl and alkoxy groups include a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a sec-butyl group, a butyl group, an amyl group, a sec-amyl group, a t-amyl group, an α,α -dimethylbenzyl group, an octyloxycar- 50 bonylethyl group, a methoxy group, an ethoxy group, an octyloxy group and an aryl group.

As for the aryl and aryloxy groups represented by R_1 , R₂ and R₃, phenyl and phenyloxy groups may preferably be used, and they may have substituents. Among 55 them, a phenyl group, a 4-t-butylphenyl group and a 2,4-di-t-amylphenyl group may be exemplified.

Among the groups represented by R₁ and R₂, a hydrogen atom, an alkyl group, an alkoxy group, an aryl group and, particularly, a hydrogen atom, an alkyl 60 group and an alkoxy group may preferably be used.

Among the groups represented by R₃, a hydrogen atom, a halogen atom, an alkyl group and an alkoxy group may preferably be used and, inter alia, a hydrogen atom, an alkyl group and an alkoxy group may 65 more preferably be used.

In order to liquidify the groups represented by R₁, R₂ and R₃ at an ordinary temperature, at least one of the

The liquid UV absorbents relating to the invention can be used, at an ordinary temperature, with a solid Uv absorbent in combination. In this case, the solid UV absorbent may be mixed therein in any mixing proportion, however, an amount of the liquid UV absorbent to be mixed in at an ordinary temperature is, preferably, not less than 10% by weight to the whole UV absorbent used and, more preferably, not less than 30% by weight thereto.

Such solid UV absorbents applicable to the invention at an ordinary temperature are allowed to take any preferable structures, provided, they are in the solid form at an ordinary temperature of 25° C.

However, from the viewpoint of the light fastness of the solid UV absorbent of its own, the solid 2-(2'hydroxyphenyl) benzotriazole type UV absorbents represented by the foregoing formula a should particularly be preferable to be used.

The typical examples of the solid UV absorbents will be given below:

$$R_3$$
 N
 N
 R_3
 R_3

Exemplified compound No.	R ₁	R ₂	R3
UV-1S UV-2S UV-3S UV-4S UV-7S UV-7S UV-9S UV-10S UV-11S UV-12S UV-13S UV-14S	-H -H -H -C4H9(t) -C4H9(t) -C4H9(t) -C5H11(t) -C4H9(sec) -C5H11(t) -H -C4H9(sec) -C5H3 -C5H11(t)	-H -CH ₃ -C ₄ H ₉ (t) -C ₄ H ₉ (t) -CH ₃ -C ₄ H ₉ (t) -C ₅ H ₁₁ (t) -C ₄ H ₉ (t) -C ₅ H ₁₁ (t) -C ₈ H ₁₇ (t) -C ₄ H ₉ (t) -C ₅ H ₁₁ (t)	-H -H -H -H -Cl -Cl -Cl -CsH ₁₁ (t) -H -H -H -H -H
UV-15S	-C ₅ H ₁₁ (t)	-0-	-CH ₃
UV-16S UV-17S	—Н —Н	-C ₁₂ H ₂₅ -OC ₈ H ₁₇ (sec)	—Н —ОСН ₃
UV-18S	-C4H9(t)	C ₄ H ₉ (t)	
UV-19S	-C ₅ H ₁₁ (t)		-OCH3

The total amount of the UV absorbents relating to the invention can be used in any amount. They may be used, for example, in a proportion within the range of $0.1 \sim 300\%$, preferably, $1 \sim 200\%$ and, more preferably, $45 \sim 100\%$, each by weight to the weight of the binders of a photographic component layer containing the UV absorbent.

Each of the UV absorbents may be added into any photographic component layers. In the case of adding it 50 into a non-light-sensitive layer, it is preferable to add it into a layer arranged farther from a support than a silver halide emulsion layer arranged nearest from the support and it is particularly preferable to add it into a layer arranged farther from the support than a silver halide 55 emulsion layer arranged farthest from the support. Also in the case of adding it into a silver halide emulsion layer, it is preferable to add it into a silver halide emulsion layer arranged farthest from the support.

A total amount of gelatin to be contained in a silver 60 halide photographic light-sensitive material of the invention is not more than 7.6 g/m² and, preferably, within the range of 5.0 g/m² to 7.6 g/m².

The silver halide grains of the invention are, preferably, to have a silver chloride content of not less than 90 65 mol %, a silver bromide content of not more than 10 mol % and a silver iodide content of not more than 0.5 mol %. More preferably, the silver halide grains of the

invention are to comprise silver chlorobromide having a silver bromide content within the range of 0.1 to 2 mol %.

The silver halide grains of the invention may be used independently or in the mixture thereof with the other silver halide grains having the different compositions. It is also allowed to use them in the mixture thereof with silver halide grains having a silver chloride content of not more than 10 mol %.

In a silver halide emulsion layer containing silver halide grains of the invention having a silver chloride content of not less than 90 mol %, the silver halide grains, which have a silver chloride content of not less than 90 mol % to the whole silver halide grain contained in the emulsion layer, are to be in a proportion of not less than 60% by weight and, preferably, not less than 80% by weight, each to the weight of the emulsion layer.

The composition of the silver halide grains of the invention may be either uniform all through from the inside of the grains to the outside thereof or different in the compositions between the inside and the outside of the individual grains. In the latter case, the compositions thereof may be varied either continuously or discontinuously from the inside to the outside of the grains.

There is no special limitation to the grain-sizes of the silver halide grains of the invention. However, taking other photographic characteristics such as rapid processability and sensitivity into consideration, the grain-sizes thereof are within the range of, preferably, $0.2 \sim 1.6 \, \mu m$ and, more preferably, $0.25 \sim 1.2 \, \mu m$. The grain-sizes can be measured in a variety of methods generally applicable to the technical fields of the art.

The typical methods thereof are detailed in, for example, Loveland, 'Particle Size Analyses', A.S.T.M. Symposium on Light Microscopy, 1955, pp. 94-122, and Mees and James, 'A Theory of Photographic Process', 3rd ed., MacMillan Publishing Company, 1966, Chapter

The above-mentioned grain-sizes may be measured by using the projective areas or approximate values of grain-sizes. When the grains are substantially uniform in shape, the considerably precise grain-size distribution may be expressed in terms of the grain-sizes or projective areas thereof.

The grain-size distribution of the silver halide grains of the invention may be either in a polydisperse type or in a monodisperse type. For the grain-size distribution of the silver halide grains, monodisperse type silver halide grains having a variation coefficient of not more than 0.22 and, particularly, not more than 0.15 are preferred. Herein, the variation coefficient is a coefficient expressing a range of grain-size distribution, and it can be defined by the following equations:

Variation coefficient
$$(S/r) = \frac{\text{Standard deviation of grain-size distribution}}{\text{Average grain-size}}$$

Standard deviation of grain-size distribution $(S) = \sqrt{\frac{\sum (r - ri)^2 ni}{\sum ni}}$

Average grain-size $(r) = \frac{\sum niri}{\sum ni}$

wherein ri represents the grain-size of an individual grain; and ni represents the number of the individual

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grain. The term, 'grain-size', used herein means a diameter of a silver halide grain when it is in the globular form, and a diameter of a circular image converted from the projective image of a silver halide grain when it is in the cubic form or any other forms than the globular 5 form.

The silver halide grains applicable to the emulsions of the invention may be those prepared in any one of an acidic method, a neutral method and an ammoniacal method. The grains may be grown either at a time or 10 after preparing seed grains. The method of preparing the seed grains and the method of growing the grains may be either the same with or the different from each other.

A soluble silver salt may be reacted with a soluble 15 halogen salt in any one of a normal precipitation method, a reverse precipitation method, a simultaneous precipitation method and the combinations thereof. Among the methods, the simultaneous precipitation method is preferably used. As one of the simultaneous 20 precipitation methods, a pAg-controlled double-jet method as detailed in Japanese Patent O.P.I. Publication No. 54-48521/1979 may also be used.

Silver halide solvents such as thioether may also be used, if required. Further, a mercapto group-containing 25 compound, a nitrogen-containing heterocyclic compound or compounds such as a sensitizing dye may also added either when or after producing silver halide grains.

Silver halide grains relating to the invention may 30 have any configurations. One of the preferable examples of the grains is a cubic grain having a {100} plane as the crystal face thereof.

Further, octahedral, tetradecahedral or dodecahedral grains may also be used. These grains may be produced 35 in the methods detailed in, for example, U.S. Pat. Nos. 4,183,756 and 4,225,666, Japanese Patent O.P.I. Publication No. 55-26589/1980, Japanese Patent Examined Publication No. 55-42737/1980, and The Journal of Photographic Science, 21, 39, 1973.

Still further, the grains having twin-crystal faces may also be used. As for the silver halide grains relating to the invention, grains having a single configuration and grains having a mixture of various configurations may also be used.

In a process of forming and/or growing the silver halide grains applicable to the emulsions of the invention, metal ions are added into the grains by making use of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt or the complex salts thereof, a rhodium 50 salt or the complex salts thereof, or an iron salt or the complex salts thereof, so that the metal ions may be contained in the grains and/or on the surfaces of the grains. Further, reduction-sensitizing nuclei may be provided to the inside of the grains and/or onto the 55 surfaces of the grains by putting the grains in a suitable reducible atmosphere.

From the emulsions of the invention containing silver halide grains -hereinafter referred to as the emulsion of the invention-, any needless soluble salts may be re- 60 moved after growing the silver halide grains. Or, the needless soluble salts may remain contained in the emulsions of the invention. In the case of removing the needless soluble salts, they may be removed in the method detailed in, for example, Research Disclosure, No. 65 17643.

The silver halide grains applicable to the emulsions of the invention may be those mainly forming a latent image either on the surfaces thereof or to the inside of the grains. Among these grains, those mainly forming an latent image on the surface thereof are preferably used.

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The emulsions of the invention may be sensitized in any ordinary methods.

The silver halide emulsions of the invention may be optically sensitized to a desired wavelength region with a sensitizing dye. Such sensitizing dyes may be used independently or in combination. It is allowed that the emulsions may contain not only the sensitizing dye, but also a dye having no spectral sensitizing function in its own or a compound substantially incapable of absorbing any visible rays of light, that is, a so-called supersensitizer capable of enhancing the sensitizing function of the foregoing sensitizing dye.

Further, the above-mentioned sensitizing dyes may be used not only for their own intrinsic spectral-sensitization but also for the adjustments of gradations and developments.

The sensitizing dyes applicable thereto include, for example, a cyanine dye, a melocyanine dye, a compound cyanine dye, a compound melocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye and a hemioxanol dye.

For the purposes of preventing a light-sensitive material from being fogged in the course of preparing, storing or photographically processing a light-sensitive material and keeping the photographic characteristics of the light-sensitive material stable, an antifoggant or a stabilizer may be added into the emulsions of the invention, during a chemical ripening process, when completing the chemical ripening process, and/or in the course between the time of completing the chemical ripening process and the time of coating the silver halide emulsion.

As for the binders for the silver halide emulsions of the invention, gelatin is advantageously used. It is also allowed to use hydrophilic colloids including, for example, a gelatin derivative, a graft polymer of gelatin and other high molecular compounds, and, besides, a protein, a sugar derivative, a cellulose derivative, and a synthetic hydrophilic high molecular substance such as a monomer or copolymer.

In the invention, the yellow dye forming couplers represented by the following formula XI may preferably be used.

wherein R₁ represents an alkyl group, a cycloalkyl group or an aryl group; and R₂ represents an alkyl group, a cycloalkyl group, an acyl group or an aryl group;

R₃ represents an atom or a group capable of being substituted for a benzene ring; n is an integer of 0 or 1; R₄ represents an organic group containing one coupling group having a carbonyl or silfonyl unit; J represents

$$-NCO- \text{ or } -CON-.$$
 R_5
 R_5

in which R₅ represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; and X represents a group capable of being split off upon reaction with the oxidized products of a color developing agent.

The yellow couplers represented by Formula XI will further be detailed.

The alkyl groups represented by R₁ include, for example, a methyl group, an ethyl group, an isopropyl group, a t-butyl group and a dodecyl group. The alkyl 15 groups represented by R₁ further include those having substituents such as a halogen atom, an aryl group, an alkoxy group, an aryloxy group, an alkylsulfonyl group, an acylamino group, and a hydroxyl group.

The cycloalkyl groups represented by R₁ include, for 20 example, a cyclopropyl group, a cyclohexyl group, and an adamantyl group.

The aryl groups represented by R₁ include, for example, a phenyl group.

The preferable groups represented by R_1 include, for 25 nitrile group. \sim X represent

The alkyl and cycloalkyl groups each represented by R₂ include, for example, the same groups as represented by R₁. The aryl groups represented by R₂ include, for example, a phenyl group.

The alkyl, cycloalkyl and aryl groups each represented by R₂ include those having the same substituents as in R₁.

The acyl groups include, for example, an acetyl group, a propionyl group, a butyryl group, a hexanoyl 35 group and a benzoyl group.

Among the groups represented by R₂, alkyl groups and aryl groups are preferable and, inter alia, alkyl groups are particularly preferable.

There is no special limitation to the groups capable of 40 being substituted for a benzene ring. however, they include, for example; halogen atoms such as a chlorine atom; alkyl groups such as an ethyl group, an i-propyl group and a t-butyl group; alkoxy groups such as a methoxy group; aryloxy groups such as a phenoxy 45 group; acyloxy groups such as a methylcarbonyloxy group and a benzoyloxy group; acylamino groups such as an acetamido group and a benzamido group; carbamoyl groups such as an N-methylcarbamoyl group and an N-phenylcarbamoyl group; alkylsulfonamido groups 50 such as an ethylsulfonamido group; arylsulfonamido groups such as a phenylsulfonamido group; sulfamoyl groups such as an N-propylsulfamoyl group and an N-phenylsulfamoyl group; and imido groups such as a succinimido group and a glutarimido group.

In Formula XI, R4 represents an organic group containing one coupling group having a carbonyl or sulfonyl unit. The groups each having a carbonyl unit include, for example, an ester group, an amido group, a carbamoyl group, a ureido group and a urethane group. 60 The groups each having a sulfonyl unit include, for example, a sulfon group, a sulfonamido group, a sulfamoyl group and an aminosulfonamido group.

represented by J, the alkyl groups represented by R₅ include, for example, a methyl group, an ethyl group, an isopropyl group, a t-butyl group and a dodecyl group. The aryl groups represented by R₅ include, for example, a phenyl group and a naphthyl group.

The alkyl and aryl groups each represented by R5 also include those having substituents. Such substituents shall not be limitative, but include, typically; halogen atoms such as a chlorine atom; alkyl groups such as an ethyl group and a t-butyl group; aryl groups such as a phenyl group, a p-methoxyphenyl group and a naphthyl group; alkoxy groups such as an ethoxy group and a benzyloxy group; aryloxy groups such as a phenoxy group; alkylthio groups such as an ethylthio group; arylthio groups such as a phenylthio group; alkylsulfonyl groups such as a β -hydroxyethylsulfonyl group; arylsulfonyl groups such as a phenylsulfonyl group;and, besides, acylamino groups such as an acetoamido group and a benzamido group; carbamoyl groups such as a carbamoyl group, an N-methylcarbamoyl group and an N-phenylcarbamoyl group; acyl groups; sulfonamido groups: sulfamoyl groups such as a sulfamoyl group, an N-methylsulfamoyl group and an N-phenylsulfamoyl group; and, further, a hydroxyl group and a

X represents a group capable of being split off upon reaction with the oxidized products of a color developing agent. The groups include, for example, those represented by Formula XII or XIII given below:

wherein R₆ represents an aryl or heterocyclic group including those having substituents.

wherein Z₁ represents the group consisting of non-metal atoms necessary to form a 5- or 6-membered ring in association with a nitrogen atom. Such atomic groups necessary to form the non-metal atom group include, for example, methylene, methine, substituted methine,

$$c=0, -NR_8$$

in which R₈ is synonymous with the foregoing R₅, —N=, —O—, —S— and —SO₂—.

The 2-equivalent yellow couplers represented by the foregoing Formula I are allowed to form a bis-substance upon coupling to the position of R₁, R₃ or R₄.

The preferable yellow couplers of the invention are represented each by Formula XIV given below:

OR₂ Formula XIV
$$(R_3)_n$$

$$X_1$$

$$J-R_7-P-R_8$$

wherein R₁, R₂, R₃ and J represent each the same groups represented by R₁, R₂, R₃ and J denoted each in Formula Xl; n is an integer of 0 or 1; R₇ represents an

alkylene group, an arylene group, an alkylenearylene group, an arylenealkylene group or $-A-V_1-B-$ in which A and B represent each an alkylene group, an arylene group, an alkylenearylene group or an arylenealkylene group, and V_1 represents a divalent coupling group; R_8 represents an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; P represents a coupling group having a carbonyl or sulfonyl unit; and X_1 is synonymous with X denoted in Formula XI.

The alkylene groups represented by R₇ include, for example, a methylene group, an ethylene group, a propylene group, a butylene group and a hexylene group, and they also include those having substituents. Those substituted with alkyl groups include, for example, each group of methylmethylene, ethyl-ethylene, 1-methylethylene, 1-methylethylene, 2-decyl-ethylene and 3-hexyl-propylene, and 1-benzyl-ethylene. Those substituted with aryl groups include, for example, each group of 2-phenyl-ethylene and 3-naphthylpropylene.

The arylene groups include, for example, a phenylene group and a naphthylene group.

The alkylenearylene groups include, for example, a methylenephenylene group, and the arylenealkylene groups include, for example, a phenylenemethylene 25 group.

The alkylene, arylene, alkylenearylene or arylenealkylene groups each represented by A or B are the same groups as the alkylene, arylene, alkylenearylene or arylenealkylene groups each represented by R7 denoted 30 in the foregoing Formula XIV. The divalent coupling groups represented by V1 include, for example, the groups of —O— and —S—. Among the alkylene, arylene, alkylenearylene, arylenealkylene and —A—V1—B— groups each represented by R7, alkylene groups 35 are particularly preferred.

The alkyl groups each represented by R₈ include, for example, an ethyl group, a butyl group, a hexyl group, an octyl group, a dodecyl group, a hexadecyl group and an octadecyl group, and these alkyl groups may be straight-chained or branched. The cycloalkyl groups include, for example, a cyclohexyl group. The aryl groups include, for example, a phenyl group and a naphthyl group. The heterocyclic groups include, for example, a pyridyl group.

The alkyl, cycloalkyl, aryl and heterocyclic groups each represented by R₈ also include those having substituents.

There is no special limitation to such substituents, and they include the same groups as the substituents given in the foregoing R₅, provided, however, it is not preferred for a substituent of R₅ to use an organic group having a dissociative hydrogen atom such as a phenolic hydrogen atom having a pKa value of not higher than 9.5.

In the foregoing Formula XIv, P represents a coupling group having a carbonyl or sulfonyl unit or, preferably, a group represented by the following group XV:

-continued Group XV

wherein R and R' represent each a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group, provided, R and R' may be the same with or the different from each other.

The groups represented by R and R' include, for example, the same groups as given by the foregoing R₅, and they also include those having substituents. Among them, one of the preferable groups represented by R and R' is a hydrogen atom.

In Formula XIV, X represents a coupling split-off group, and the groups preferably represented by X include, for example, those represented by Formulas XVI through XXII each given below:

wherein R₉ represents a carboxyl group, an ester group, an acyl group, an alkylsulfonyl group, an arylsulfonyl group, a hydroxyl group or the same substituents as the groups given by the foregoing R₃; and l is an integer of 1 to 5, provided, when l is not less than 2, R₉s may be the same with or the different from each other.

Formula XVII

$$N$$
 R_{11}
 R_{10}

Formula XVIII

 N
 R_{10}

$$R_{10}$$
 N
 N
 R_{11}
 N
 R_{11}

wherein R₁₀ and R₁₁ represent each a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an aryl group, a heterocyclic group, an alkoxycarbonyl group, an aryloxycarbonyl group, an amino group, an acylamino group, an alkylsulfonyl group, an arylsulfonyl group, an alkylsulfonamido group, an arylsulfonamido group, an alkylsulfonamido group, an arylsulfonamido group, a carboxyl group, and the above-given groups each having substituents.

R₁₀ and R₁₁ may form a ring.

Formula XX
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Formula XX
$$\begin{array}{c|c}
N & N & N \\
N & N & N \\
R_{12} & Z_3
\end{array}$$

wherein Z_2 and Z_3 represent each a hetero atom such as an oxygen atom, and R_{12} , R_{13} and R_{14} represent each 10 the same groups as represented by the foregoing R_{10} and R_{11} .

R₁₅ represents an alkyl group, an aryl group, an alkyl-carbonyl group, an arylcarbonyl group, an alkylsulfonyl group, and an arylsulfonyl group.

wherein Y represents a hetero atom such as —NH—, —N—, —O— and —S—, a sulfonyl group, a carbonyl group, or a carbon atom represented by

and Z₄ represents the group consisting of non-metal atoms necessary to form a 5- or 6-membered ring in association with

The atomic group necessary to form the group consisting of non-metal atoms may be given by the same groups as in the foregoing Z_1 .

R₁₆, R₁₇ and R₁₈ represent each the same groups as represented by R₁₀ and R₁₁. R₁₆, R₁₇ and R₁₈ may also form a ring in association with a part of Z₄.

The 2-equivalent yellow couplers represented by the foregoing Formula XIV are allowed to form a bis-substance by coupling them to R₁, R₃ or a ballast group.

Next, the typical examples of the yellow couplers applicable to the invention, which are represented by Formula XI, will be given below. It is, however, to be understood that the invention shall not be limited thereto.

			. •	•			•	
-C	a	n	1	n	11	0	a	

<u></u>	· · · · · · · · · · · · · · · · · · ·	OR ₁	
		// \	3rd position
-		R ₁ COCHCONH— Z 6th position	4th position
XI-5	(t)C ₄ H ₉ —	-cH ₃	N = Cl
			-N
			\ <u> </u>
XI-6	(t)C ₄ H ₉ —	-CH ₃	OC ₄ H ₉
•)— N— \\
			o" \/
XI-7	(t)C ₄ H ₉ —	$-C_3H_7(iso)$	O\\OC_*Hc
			$-N$ OC_2H_5
			$\rightarrow N-\langle N-\langle N-\langle N-\langle N-\langle N-\langle N-\langle N-\langle N-\langle N-\langle$
			o" \/
XI-8	(t)C ₄ H ₉ —	—CH ₃	
		•	$-o-\left\langle \begin{array}{c} \\ \\ \\ \end{array} \right\rangle - so_2 - \left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle - och_2 - \left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle$
X1-9	(t)C ₄ H ₉ —	$-C_{12}H_{25}$	
	· · · · · · · · · · · · · · · · · · ·		_o_\\so_2_\\он
XI-10	(t)C ₄ H ₉ —	$-C_{18}H_{37}$	
			CONH— CONH— N M M M M M M M M M M M M
			—N ——/
XI-11	(t)C ₄ H ₉ —	—CH ₃	0
			$N-C_6H_{13}$ $-N$
) N
			o" \/
XI-12	(t)C ₄ H ₉ —	-C ₄ H ₉	0
·			—N
			\rightarrow N-CH ₂ -
		•	o" \/
XI-13	(t)C ₄ H ₉ —	—CH ₃	O,,
			»— N—СН ₂ ——
			o/ N/
			•

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		R ₁ COCHCONH————————————————————————————————	3rd position 4th position 5th position
XI-14	(t)C ₄ H ₉ —	-CH ₃	-N -CI
X1-15	(t)C ₄ H ₉ —	-CH ₃	
XI-16	(t)C ₄ H ₉ —	-CH ₃	$NSO_2 - CH_3$ $-N$ $N = C_3H_7(iso)$
XI-17	CH C ₂ H ₅ OCH ₂ C— I CH ₃	-CH ₃	$ \begin{array}{c c} O \\ N \\ N \\ N \\ N \\ N \end{array} $ $ \begin{array}{c} CH_3 \\ N \\ N$
XI-18	(t)C ₄ H ₉ —	-CH ₃	-0 $-SO_2$ $-OCH_2$
XI-19	(t)C ₄ H ₉ —	-CH ₃	$-O$ $-COOC_2H_5$
X1-20	(t)C ₄ H ₉ —	-C ₁₂ H ₂₅	$ \begin{array}{c} OC_6H_{13} \\ \nearrow N \\ O \\ O \end{array} $
X1-21	(t)C ₄ H ₉ —	-C ₂ H ₅	COOCH ₃ -N NH O
XI-22	CH ₃ OC- CH ₃	—C ₄ H ₉	$COOC_6H_{13}$ N
XI-23	(t)C ₅ H ₁₁	-C ₂ H ₅	H

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	•	OR ₁	\sim 3rd position
		R ₁ COCHCONH—	4th position
	•	Z 6th position	/
XI-24	(t)C ₄ H ₉ —	-CH ₃	
• • • • • • • • • • • • • • • • • • •	(-) — 4)		N — N O
	•		
•			V= N
XI-25	(t)C ₄ H ₉ —	$-C_{16}H_{37}$	
•			$-o-\langle \rangle - so_2-\langle \rangle - oH$
			} /
			Ci
XI-26	(t)C ₄ H ₉ —	-CH ₃	O CH ₃
)—————————————————————————————————————
			—N .
			N-CH ₂ OH
			O
XI-27	(t)C ₄ H ₉ —	-CH ₃	/= N
			-N
			$\sim N-CH_3$
	-		O
X1-28	(t)C ₄ H ₉ —	—CH ₃	0,
			\sim N-CH ₂ - \sim CH ₃
			· - N
		•	~ ~ ~ »
			O` \/
XI-29	ÇH ₃	$-C_{12}H_{25}$	COOC ₂ H ₅
	_\c_1		\rightarrow COOC ₂ H ₅
	CH ₃		-N
	•		√ — N
XI-30	$(t)C_5H_{11}$	— CH ₃	O CH ₃
			CH ₃
			-N
			NHCOCH ₃
XI-31	(t)C ₄ H ₉ —	$-cH_3$, s
			-N'
			ö
XI-32	(t)C ₄ H ₉ —	—CH ₃	O
			$\sim N-C_6H_{13}$
			N=N

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		OR ₁ R ₁ COCHCONH	3rd position 4th position
		Z 6th position	
XI-33	(t)C ₄ H ₉ —	-CH ₃	
X1-34	(t)C ₄ H ₉ —	————COOC ₂ H ₅	
XI-35	(t)C ₄ H ₉ —	-C ₄ H ₉	-N CI
XI-36	(t)C ₄ H ₉ —	-CH3	-o- SO ₂ — ОН
X1-37	(t)C ₄ H ₉ —		OC_4H_9 $-N$ N
XI-38	(t)C ₅ H ₁₁ —	O -CCH ₃	$ \begin{array}{c c} O & C_2H_5 \\ N-CHCH_3 \\ -N & N \end{array} $
XI-39	(t)C ₄ H ₉ —	O II —CC ₂ H ₅	$ \begin{array}{c} O \\ -N \\ O \\ N \end{array} $ $ \begin{array}{c} CH_2COOC_2H_5 \\ O \\ \end{array} $
XI-4 0	(t)C ₄ H ₉ —	-CH ₃	OC_2H_5 N N

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-00	ntii	nue	1

·		OR ₁	-_3rd position
		R ₁ COCHCONH—	4th position
		Z 6th position —	5th position
XI-41	(t)C ₄ H ₉ —	-CH ₃	
X1-42	(t)C ₄ H ₉ —	-CH ₃	$ \begin{array}{c c} O \\ N - C_2H_5 \\ -N \\ N - CH_2 - O \end{array} $
X1-43	(t)C ₄ H ₉ —	-CH ₃	CONH(CH ₂) ₂ OH
X1-44	SO ₂ CH ₂ C- CH ₃	-C ₂ H ₅	$N=N$ $-N$ $N-C_4H_9(iso)$
XI-45	(t)C ₄ H ₉ —	——————————————————————————————————————	$\begin{array}{c} -N \\ $
X1-46	CH ₃ O-CH ₂ C- CH ₃ CH ₃	-CH ₃	$ \begin{array}{c c} O \\ N - C_6H_{13} \\ O \\ N \end{array} $
XI-47	(iso)C ₃ H ₇ —	C ₄ H ₉	-O $-O$ $-O$ $-O$ $-O$ $-O$ $-O$ $-O$
X1-48		CH ₃	O CH_3 CH_3
XI-49	H	-CH ₃	COOCH ₃ COOCH ₃

XI-6

$\cdot cc$	nt	m	ued

			-continued	
	· · · · · · · · · · · · · · · · · · ·		OR ₁	
		T3	3rd position	•
	,	K ₁	COCHCONH— Ath position Sth position	
XI-50	(t)C ₄ H ₉ —	······································	Z 6th position — 5th position —CH ₃	
		•	-0	
	•			
W1 61		•	-CH ₃	
XI-51		•	\sim N-C ₄ H ₉	
	· \/		-N	•
			$\rightarrow N-$	>
XI-52			$-C_2H_5$ CH_3	CH ₃
	/	-	-0 -0 -0 -0	OH
	\/			
XI-53			$-C_{16}H_{33}$	
711-00			-N	
	/		$\rightarrow N$	
			conh—()	•
		4 - 1	5th position	6th position
No. XI-1	3rd position —H	4th position —H	Jui position	H
	·		NHCO(CH ₂) ₃ O $-$ C ₅ H ₁₁ (t)	-
				-
			$C_5H_{11}(t)$	
XI-2	—H	- н	ÇH ₃	—н
			$-\text{CONHCHCOO(CH}_2)_2\text{O}-\left\langle \begin{array}{c} \\ \\ \\ \end{array} \right\rangle -\text{OC}_{12}\text{H}_2$	25
			\/	
XI-3	- -н	—H	CH ₃	— H
			-NHCOCHCH ₂ SO ₂ C ₁₂ H ₂₅	
XI-4 -	— н	− H	$C_5H_{11}(t)$	—H
			-NHCO(CH ₂) ₂ COO	
			$-NHCO(CH2)2COO- \left\langle \right\rangle -C5H11(t)$	
XI-5	- н	— н	ÇH ₃	- н
		. — 	-N-COCHCH ₂ SO ₂ C ₁₈ H ₃₇	
			ĊH ₂	

-NHCO(CH₂)₂CONH₁₂H₂₆

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<b>-6</b> 'C }5 f l	467676771
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		D	3rd position  4th position	
		· · · · · · · · · · · · · · · · · · ·	COCHCONH—  Ath position  Sth position  Sth position	
XI-7	<b>-</b> Н	H		<b>—</b> Н
			$-\text{CONH}(\text{CH}_2)_3\text{CONH}-\left\langle -C_{12}H_{25}\right\rangle$	
	· 			
XI-8	H	—H		<del>-</del> Н
			-conh-\(\)-\NHCOC ₁₂ H ₂₅	
<b>3</b> /1 0	· •	T.T		<b>—</b> н
X1-9	<b>—</b> н	H	-CONHCHCH ₂ SO ₂ C ₂ H ₅       CH ₃	1.1
<b>XI</b> -10	—H	— H	ÇH ₃	—н
211-10	••		-NHCOCCH ₂ SO ₂ C ₄ H ₉	
			CH ₃	
XI-11	<del></del> Н	<b></b> H		<b>—</b> Н
			-NHCOCHNHCO( )-OC ₁₂ H ₂₅	
	•		CH ₃	
XI-12	<b>—</b> Н	<del></del> н		—- H
			-NHCOCHO- $\langle$	
XI-13	<b>—</b> Н	<del></del> Н	-CONH(CH ₂ ) ₂ NHSO ₂ C ₁₂ H ₂₅	—H
XI-14	—н	— H	-CONHCHCH ₂ SO ₂ CH ₂ CHC ₈ H ₁ ⁷	—H
<del>-</del>			COMMENT 2502CH28H47 	
XI-15	<del>-</del> н	—H	· · · · · · · · · · · · · · · · · · ·	<b>-</b> н
			-SO2NH(CH2)3O-  C5H11(t)	
			\/	
		•	$C_5H_{11}(t)$	
XI-16	<del></del> Н	— H		<del>-</del> н
			-NHCOCH(CH ₂ ) ₂ NHCO- $\left\langle \begin{array}{c} \\ \\ \\ \\ \end{array} \right\rangle$ -OC ₁₂ H ₂₆ CH ₃	
XI-17	—H	<b>—</b> Н	-NHCO(CH ₂ ) ₁₀ COOC ₂ H ₅	—Н
XI-17 XI-18	—Н	—н		<b>—</b> н
		<b></b>	$-\text{CONH}$ $-\text{SO}_2\text{NHC}_{12}\text{H}_{25}$	<b></b>
XI-19	<del>-</del> н	H		<b>-</b> Н
			-мнсосно-	
			$C_{12}H_{25}$	
	-aa-		$C_4H_9(t)$	
XI-20	—H	<b>—</b> Н	NHCO(CH ₂ ) ₂ SO ₂ NHCH ₂ CHC ₄ H ₉	—H
			$C_2H_5$	

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			OP.	
		•	$\sum_{\lambda=0}^{\infty} 3rd$ position	
		R ₁ COCH	CONH—( ) 4th position	
	·	Ż	5th position 5th position	······································
XI-21	<b>-</b> Н	· —Cl	OC4H9	—H
			CH ₃	
			-NHCOCCH ₂ SO ₂ -	
			CH ₃	
			C ₈ H ₁₇ (t)	
				11
XI-22	—н	—H	-NHSO ₂ C ₁₆ H ₃₃	H
XI-23	—Н	H	CH ₃	<b>-</b> H
		•	$-NHCOCH(CH_2)NHSO_2$ $\longrightarrow$ $-OC_5H_{10}$	
			• • •	—н
XI-24	<del>-</del> Н	—H		
			$-NHSO2(CH2)3O- \langle \rangle -C5H11(t)$	
				•
			$C_5H_{11}(t)$	
XI-25	—H	— H	-NHCO(CH ₂ ) ₂ NHSO ₂ N-CH ₃	<del>-</del> Н
A1-23	11	**- ·		•
				•
XI-26	<b>—</b> н	<b>—</b> Н	$OC_{12}H_{26}$	. — <b>н</b>
			$-\text{CONH}(\text{CH}_2)_4\text{NHCO}$	
			\(	
	•		CH ₃	
<b>4.1 57</b>	7 T	—- H	CONTICUOU.CO.NUCU.	. —н
XI-27	<del></del> Н	. ——11	CONHCHCH ₂ SO ₂ NHC ₁₂ H ₂₆	
		•	$C_6H_{13}$	
XI-28	<b>-</b> н	<b>—</b> H	$-COOC_{12}H_{25}$	<b>—</b> н
XI-29	H	H	$C_2H_5$	Н
			-NHCO(CH ₂ ) ₃ NHCONHCH ₂ CHC ₄ H ₉	
		<b>-</b>		<del></del> Н
XI-30	<del></del> Н	—H		4.4
			-CONHCHCH ₂ CONH-\\ \>-OC ₄ H ₉	-
			C ₆ H ₁₃	
XI-31	<b>—</b> Н	—H	$-COOC_{18}H_{35}$	—н
				<b>—</b> Н
X1-32	<b>—</b> H	—H	-NHCO(CH ₂ ) ₃ NHCOCH ₂ CHC ₆ H ₁₃	**
			C ₈ H ₁ 7	
XI-33	—н	—C]	CH ₃ C ₁₂ H ₂₅	—H
		•	-NHCOCCH2NHCON	
			$CH_3$ $C_2H_5$	
				<del></del> Н
	<del>-</del> Н	<del>-</del> Н		<b>1</b> 1
XI-34	· · · · · · · · · · · · · · · · · · ·			
XI-34	· · · · · · · · · · · · · · · · · · ·		-CONHCH2CHSO-C18H37	

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		31	52	
·	<u>-</u>		-continued	<del></del>
	-		OR1	
			3rd position	
		R ₁ COCHCON	\ /	
·	<del>,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</del>	Z 6th po	osition5th position	<del></del>
XI-35		-NHCOCHSO ₂ NHC ₁₂ H ₂₅	—Cl	—H
		C ₁₆ H ₃₃		
XI-36	-н	—C1	·	<del>-</del> н
			NILCO(CIL ) NILCO	
			$-NHCO(CH_2)_2NHCO$ $-C_{12}H_{26}$	
			\ <del></del>	**
XI-37	—H	—H	CH ₂	H
	•	-	-CONHCCH ₂ CONH-\(\bigc\)-OC ₁₂ H ₂₅	
			CH ₂	
XI-38	<b>—</b> н	$-och_3$	$OC_{12}H_{26}$	—H
			-NHCOCH(CH2)2NHSO2 - CH3	•
XI-39	<del>-</del> Н	—H	-COOCHCOOC ₁₂ H ₂₅	—H
			CH ₃	
<b>XI-4</b> 0	<b>—</b> н	— H	CH ₃	—H
			-CONHC(CH ₂ ) ₂ COO	
•			CH ₃	
XI-41	<b>-</b> н	ÇH3	· —OCH ₃	<del>-</del> Н
		-CONH(CH ₂ ) ₄ NHSO ₂ CHC ₄ H ₉		
XI-42	<del>-</del> н	— H		-н
			$-\text{CONH}$ $-\text{SO}_2\text{NHC}_{12}\text{H}_{25}$	
XI-43	<del></del> Н	— H	-COOCHCOOC ₁₂ H ₂₅	—н
			C4H9	
XI-44	<b>—</b> н	— <b>н</b>		—H
<b>.</b>		4.4	-NHCO(CH ₂ ) ₃ CON-C ₆ H ₁₃	
			CH ₂	
XI-45	<b>—</b> Н	<b>—</b> Н	OCH ₃	<b>—</b> Н
			<u></u>	
			-CONHCHCH2SO2-	
		•	$C_2H_5$	
			C ₈ H ₁₇ (t)	•
<b>XI-4</b> 6	-н	—-H	-CONHCHCOOC ₁₂ H ₂₅	-н
			1	

1 C₂H₅

			-continued	
•		R ₁ C	OR ₁ 3rd position COCHCONH— 4th position	
	· · · · · · · · · · · · · · · · · · ·		Z 6th position 5th position	
X1-47	—-H	H	$-NHCOCHNHCOCH_2 - C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$	—H
XI-48	—н	—н	-NHCO(CH ₂ ) ₁₀ COOC ₂ H ₅	<del></del> Н
XI-49	-H	—H	-CONH(CH2)4NHSO2 - C8H17(t)	-H
XI-50	—H	-H	-NHCO(CH2)2NHCONHCH2O-C5H11(t)	-H
XI-51	<b>—</b> H	— <b>H</b>	CH ₃ -NHCOCHCH ₂ SO ₂ C ₁₂ H ₂₅	—H
X1-52	—H	-H	$-NHCOCHNHCOCH_2 - C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$	-H
XI-53	<del>-</del> н	— H	-SO ₂ NHCOC ₂ H ₅	—Н

The yellow couplers of the invention can be synthesized in any conventionally known methods. The typical synthesizing examples thereof are described in, for example, Japanese Patent O.P.I. Publication No. 63-123047/1988.

The couplers of the invention may be used in an  45  amount within the range of, normally,  $1 \times 10^{-3} \sim 1$  mol and, preferably,  $1 \times 10^{-3} \sim 8 \times 10^{-1}$  mols, each per mol of silver halide used. They may be used with any other couplers than the couplers of the invention.

The cyan dye-forming couplers preferably applicable 50 to the invention are represented by Formula XXXI given below:

wherein  $R^1$  represents an alkyl group having 2 to 6 carbon atoms;  $R^2$  represents a ballast group; and  $Z_1$  represents a hydrogen atom, or an atom or a group capable of being split off upon reaction with the oxidized products of a color developing agent.

In the cyan couplers represented by Formula XXXI, the alkyl groups each having 2 to 6 carbon atoms, repre-

sented by R¹, may be straight-chained or branched and they include those having substituents. The groups represented by R¹ include preferably an ethyl group.

The ballast groups represented by R² are organic groups each having the sizes and shapes necessary to give the molecules of a coupler a sufficient volume so as not to substantially diffuse the coupler from the layer containing the coupler into any other layers.

The preferable ballast groups are represented by the following formula:

wherein R³ represents an alkyl group having 1 to 12 carbon atoms; and Ar represents an aryl group such as a phenyl group, and such aryl groups include those 60 having substituents.

In Formula XXXI, the atoms or groups capable of being split off upon reaction with the oxidized products of a color developing agent, which are represented by Z₁, include, for example, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, a sulfonyloxy group, an acylomyloxy group, an aryloxycarbonyloxy group, an alkoxycarbonyloxy group, and those having

substituents. Among them, the preferable are a halogen atom, an aryloxy group and an alkoxy group.

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Next, the typical examples of the couplers represented by Formula XXXI will be given below. It is, however, to be understood that the invention shall not be limited thereto.

		$C1$ $R^1$ $Z_1$	NHCOR ²
Coupler No.	· R ¹	Zı	$\mathbf{R}^2$
XXXI-1	-C ₂ H ₅	—Cl	$C_5H_{11}(t)$ $-CH_2O$ $-C_5H_{11}(t)$
XXXI-2	-C ₂ H ₅	O—NHCOCH3	$C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_2H_5$
XXXI-3	—C ₃ H ₇ (i)	—CI	$-CHO - C_{15}H_{31}$
XXXI-4	$-C_2H_5$	—C1	$C_5H_{11}(t)$ $C_5H_{11}(t)$ $C_5H_{11}(t)$
XXXI-5	-C ₄ H ₉	—-F	$-CHO$ $-SO_2$ $-OH$ $-C_{12}H_{25}$
XXXI-6	$-C_2H_5$	-F	$-CHO$ $C_{12}H_{25}$ $C_{4}H_{9}(t)$
XXXI-7	$-C_2H_5$	—CI	$C_5H_{11}(t)$ $-(CH_2)_3O$ $C_5H_{11}(t)$
XXXI-8	-C ₂ H ₅	—-C)	-CHO-NHSO ₂ C ₄ H ₉ C ₁₂ H ₂₅
XXXI-9	$-C_2H_5$	—C1	$CI$ $CHO$ $CI$ $C_{12}H_{25}$ $CI$
		_	

		· Z ₁	
Coupler No.	. R ¹	Z ₁	. R ²
XXXI-10	—C ₃ H ₇ (i)	—C1	$-C_{18}H_{37}$
XXXI-11	-C ₆ H ₁₃	-C1	$C_5H_{11}(t)$
•			$-CHO - C_5H_{11}(t)$ $C_2H_5$
XXXI-12	-C ₃ H ₇	—C1	$C_5H_{11}(t)$ NHCOCHO $C_5H_{11}(t)$ $C_5H_{11}(t)$
XXXI-13	-(CH ₂ ) ₂ NHCOCH ₃	<b>—</b> Cl	$C_5H_{11}(t)$
			$-CHO - C_5H_{11}(t)$ $C_2H_5$
XXXI-14	—(CH ₂ ) ₂ OCH ₃	<b>—</b> C1	$C_5H_{11}(t)$
			$-CHO - C_5H_{11}(t)$ $C_2H_5$
XXXI-15	$-c_2H_5$	—C1	$C_4H_9(t)$
			$-CHO - C_4H_9(t)$ $C_4H_9$
XXXI-16	—C ₄ H ₉ (t)	-O(CH ₂ ) ₂ -SO ₂ CH ₃	$-CHO - C_9H_{19}$ $C_6H_{13}$
XXXI-17	$-C_2H_5$	—C1	Cl
			$-CHO - C_8H_{17}(t)$ $C_6H_{13}$
XXXI-18	$-C_2H_5$	—Cl	CN
			$-CHO$ $-NHSO_2CH_3$ $C_{12}H_{25}$
XXXI-19	$-C_2H_5$	—C1	$C_5H_{11}(t)$
			$-CHO - C_5H_{11}(t)$ $C_4H_9$

# -continued OH CI $R^1$ $Z_1$ NHCOR² $Z_1$ $R^2$ XXXI-20 COupler COuple

The typical examples of the cyan couplers applicable to the invention, including those given above, are detailed in, for example, Japanese Patent Examined Publication No. 49-11572/1974, and Japanese Patent O.P.I. Publication Nos. 61-3142/1986, 61-9652/1986, 20 61-9653/1986, 61-39045/1986, 61-50136/1986, 61-99141/1986 and 61-105545/1986.

The cyan couplers of the invention represented by the foregoing Formula XXXI may be used in an amount within the range of, normally,  $1 \times 10^{-3}$  mols to 1 mol 25 and, preferably,  $1 \times 10^{-2}$  mols to  $8 \times 10^{-1}$  mols, each per mol of silver halide used.

The cyan couplers of the invention may be used with any other cyan couplers than those of the invention in combination. When making such a combination use, a 30 2,5-diacylaminophenol type coupler represented by the following formula XXXIII should particularly be preferred.

wherein R⁴ represents an alkyl or aryl group; R⁵ represents an alkyl, cycloalkyl, aryl or heterocyclic group; R⁶ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; provided, R⁶ and R⁴ may form a ring in association with each other; and Z₃ represents a hydrogen atom or a group capable of being split off upon reaction with the oxidized products of an aromatic primary amine type color developing agent.

In the invention, it is preferable to make a combination use of the foregoing cyan coupler and the magenta coupler represented by Formula XXXII given below:

$$R_2$$
 $R_1$ 
 $R_2$ 
 $R_3$ 
 $N$ 
 $N$ 
 $Z_2$ 

wherein R₁, R₂ and R₃ represent each substituents other than hydrogen atom, and they may be the same with or the different from each other; Z₂ represents the group consisting of non-metal atoms necessary to form a heterocyclic ring; provided, the heterocyclic ring may have 65 a substituent; and X represents a hydrogen atom or a group capable of being split off upon reaction with the oxidized products of a color developing agent.

The magenta couplers represented by Formula XXXII may further be represented by Formulas XXXIIa through XXXIIf each given below:

In the above formulas, R₁, R₂, R₃ and X are each synonymous with R₁, R₂, R₃ and X each denoted in the foregoing Formula XXXII; and R₄, R₅, R₆, R₇, R₈, R₉ and R₁₀ represent each a substituent.

Among the magenta couplers represented by the above formulas, the preferable are the compounds represented by Formulas XXXIIa and XXXIIb and, among them, the more preferable are the compounds represented by Formula XXXIIa.

The substituents given by Formulas XXXII and XXXIIa through XXXIIf will be detailed below.

R₁~R₃ may be the same with or the different from each other, and each of them represents any one of the following atoms and the groups; namely, a hydrogen atom; halogen atoms such as a chlorine atom, a bromine atom and a fluorine atom; alkyl groups including those straight-chained or branched and substitutable alkyl groups each having 1~32 carbon atoms, such as a

methyl group, a propyl group, a t-butyl group, a hexadecyl group, a 3-(3-pentadecylphenoxy)propyl group, a 3-(2,4-di-t-amylphenoxy)propyl group, a 3-(2,4-di-tamylphenoxy)ethyl group, a 3-(4-di-t-amylphenoxy)propyl group, and a 2- $[\alpha$ -(3-t-butyl-4-hydroxyphenoxy) 5 tetradecaneamidoethyl] group; cycloalkyl groups such as a cyclohexyl group; alkenyl groups such as a propenyl group; cycloalkenyl groups; alkinyl groups; aryl groups such as a phenyl group;  $\alpha$ - or  $\beta$ -naphthyl groups; 4-methylphenyl groups; 2,4,6-trichlorophenyl 10  $4-[\alpha-(3-t-butyl-4-hydroxyphenoxy)]$ radecaneamido]-2,6-dichlorophenyl groups; heterocyclic groups such as a pyridyl group, thienyl group and a quinolyl group; acyl groups such as an acetyl group and a benzoyl group; sulfonyl groups; sulfinyl groups; 15 phosphonyl groups such as a butyloctyl phosphonyl group; carbamoyl groups; sulfamoyl groups; cyano groups; spiro-compound residual groups such as a spiro(3,3)heptane-1-yl group; cross-linking hydrocarbon compound residual groups such as a bicyclo(2,2,1)hep- 20 tane-1-yl group; alkoxy groups such as a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group and an n-butyl group; aryloxy groups such as a phenoxy group; heterocyclic oxy groups such as a 1-phenyltetrazolyloxy group; siloxy groups such as a 25 trimethylsiloxy group; acyloxy groups such as an acetyloxy group; carbamoyloxy groups; amino groups; acylamino groups such as an acetylamino group; benzamido groups; 3-(2,4-di-tamylphenoxy)butylamido groups; sulfonamido groups such as a methanesul- 30 fonamido group; imido groups such as a succinimido

group; ureido groups; sulfamoylamino groups; alkoxycarbonylamino groups such as a methoxycarbonylamino groups; aryloxycarbonylamino groups such as a phenoxycarbonylamino group; alkoxycarbonyl groups such as a methoxycarbonyl group; aryloxycarbonyl groups such as a phenoxycarbonyl group; aryloxycarbonyl groups such as a phenoxycarbonyl group; alkylthio groups such as a hexylthio group and a dodecylthio group; arylthio groups such as a phenylthio group; or heterocyclic thio groups such as a 3-pyridylthio group.

R4 through R10 represent each a hydrogen atom; alkyl groups, that is, straight-chained or branched substitutable alkyl groups each having 1 to 32 carbon atoms, including typically the same groups as given for the foregoing R₁ through R₃; aryl groups such as those given for R₁ through R₃; heterocyclic groups such as those given for R₁ through R₃; acylamino groups such as an acetylamino group; a benzamido group; a 3-(2,4di-t-amylphenoxy)butylamido group; a 3-(3pentadecylphenoxy)butylamido group; alkylamino groups such as a methylamino group, a diethylamino group and a dodecylamino group; anilino groups such as a phenylamino group, a 2-chloro -5-tetradecaneamidophenylamino group and a 4- $[\alpha$ -(3-t-butyl-4hydroxyphenoxy)tetradecaneamido]anilino group; alkoxycarbonyl groups such as a methoxycarbonyl group and a tetradecyloxycarbonyl group; alkylthio groups such as a hexylthio group and a dodecylthio group.

The typical examples of the preferable magenta couplers will be given below.

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(t)C₄H₉
N
N
N
OC₄H₉

$$C_8H_{17}(t)$$

$$(t)C_4H_9 + H_N + N_N + N_N$$

$$\begin{array}{c|c} Cl & H & \\ \hline N & N & \\ \hline N & \\ \hline N & \\ \hline CHCH_2SO_2C_{18}H_{37} \\ \hline CH_3 & \\ \end{array}$$

(t)C₄H₉

$$\begin{array}{c|c}
C1 & H \\
N & CH_3 \\
\hline
C - CH_2SO_2 - OC_{12}H_{25}
\end{array}$$
I-28

(t)C₄H₉

$$N$$
 $N$ 
 $CH_3$ 
 $C-CH_2SO_2$ 
 $CH_3$ 
 $CH$ 

Cl H N OCH₂CON(C₂H₅)₂

$$N \longrightarrow N \longrightarrow CH_{2}CH_{2}SO_{2} \longrightarrow C_{8}H_{17}(t)$$

$$\begin{array}{c|c} CH_2-CH \\ \hline \\ COOC_4H_9 \end{array} \\ \begin{array}{c} N \\ H \end{array} \\ \begin{array}{c} CH_2-CH \\ \hline \\ COOC_4H_9 \end{array} \\ \begin{array}{c} N \\ N \\ H \end{array} \\ \begin{array}{c} CH_2-CH \\ \hline \\ COOC_4H_9 \end{array} \\ \begin{array}{c} N \\ N \\ H \end{array} \\ \begin{array}{c} N \\ C_4H_9(t) \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \end{array} \\ \begin{array}{c} N \\ N \\ N \\$$

$$x:y = 50:50$$

$$(t)C_4H_9 \xrightarrow{Cl} H \xrightarrow{CH_3} OC_6H_{13}$$

$$(t)C_4H_9 \xrightarrow{N-N-N} N - N - N$$

$$(t)C_4H_9 \xrightarrow{Cl} H \xrightarrow{N-N-N} (CH_2)_2 \xrightarrow{CH_3} OC_{12}H_{25}$$

(1)C₄H₉

$$\begin{array}{c}
C_1 \\
N \\
N \\
N \\
N
\end{array}$$
(CH₂)₂SO₂

$$\begin{array}{c}
NHSO_2C_{16}H_{33} \\
N \\
N
\end{array}$$

$$(t)C_4H_9 \xrightarrow{Cl} H \\ N \longrightarrow N \longrightarrow N$$

$$(CH_2)_3 \longrightarrow NHSO_2 \longrightarrow OC_{12}H_{25}$$

$$(t)C_4H_9 \longrightarrow N \longrightarrow N$$

$$CHCH_2NHSO_2 \longrightarrow OC_8H_{17}(t)$$

$$NHSO_2 \longrightarrow C_8H_{17}(t)$$

$$C_8H_{17}(t)$$

OCH₃
OCH₃
OC₈H₁₇
OC₈H₁₇
N
N
N
N
N
$$CHCH_2SO_2$$
OC₈H₁₇
N
 $CHCH_2SO_2$ 
OC₈H₁₇
 $CHCH_2SO_2$ 
OC₈H₁₇
 $CHCH_2SO_2$ 
OC₈H₁₇
 $CHCH_2SO_2$ 
OC₈H₁₇
 $CHCH_2SO_2$ 

$$(t)C_4H_9 \longrightarrow N \longrightarrow N$$

$$CHCH_2NHSO_2 \longrightarrow OC_8H_{17}$$

$$OC_8H_{17}$$

$$OC_8H_{17}$$

$$OC_8H_{17}$$

$$OC_8H_{17}$$

$$OC_8H_{17}$$

$$OC_8H_{17}$$

$$CH_3$$

$$CHCH_2NHSO_2$$

$$CHCH_2NHSO_2$$

$$CH_3$$

$$CHCH_2NHSO_2$$

$$C_8H_{17}(t)$$

$$(t)C_4H_9 \xrightarrow{C_1} N \xrightarrow{N} N \xrightarrow{C_2H_5} C_{2}H_5$$

$$C_8H_{17}(t)$$
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$$CH_3 \qquad CI \qquad H \qquad CH_2CH_2CNNHSO_2 \qquad CH_3 \qquad N-N-N \qquad NHSO_2C_{16}H_{33}$$

The above-given couplers can be synthesized with reference to Journal of the Chemical Society, Perkin I, 1977, pp. 2047–2052, U.S. Pat. No. 3,725,067, and Japa- 50 nese Patent O.P.I. Publication Nos.59-99437/1984, 58-42045/1983, 59-162548/1984, 59-171956/1984, 60-33552/1985, 60-43659/1085, 60-172982/1985 and 60-190779/1985.

In the case of making the combination use of the cyan 55 coupler and magenta coupler, the amount of gelatin to be contained in a red light-sensitive silver halide emulsion layer of the invention is, preferably, less than 1.4 g and, more preferably, within the range of 1.0 to 1.3 g per sq. meter of the light-sensitive material used.

The amount of gelatin to be contained in a green light-sensitive silver halide emulsion layer of the invention is, preferably, not more than 1.4 g and, more preferably, within the range of 1.1 to 1.4 g per sq. meter of the light-sensitive material used.

The dye-forming couplers applicable to the invention are allowed to contain a compound capable of discharging photographically useful fragments upon coupling

reaction with the oxidized products of a developing agent, such as a development accelerator, a bleach accelerator, a developing agent, a silver halide solvent, a toner, a hardener, a foggant, an antifoggant, a chemical sensitizier, a spectral sensitizer and a desensitizer. The above-mentioned dye-forming couplers may be used with a colored coupler and/or a DIR coupler in combination, and such a DIR coupler may be replaced by a DIR compound to be used therein.

The DIR couplers and DIR compounds applicable thereto include those containing an inhibitor directly coupled to the coupling position, a timing DIR coupler, and a timing DIR compound. As for the inhibitors, those having splitting-off and diffusion properties and those having not so much diffusion property may be used, independently or in combination, to meet the applications. Further, a colorless coupler may also be used with the dye-forming couplers in combination.

In the invention, it is preferable to contain a hydroquinone type compound into a coupler-containing emulsion layer relating to the invention and/or into the 70

adjacent layers thereto. The hydroquinone type compound may be added in any amount thereinto, however, it is added in an amount within the range of, preferably,  $1\times10^{-6}$  to  $1\times10^{-2}$  mols/m² and, more preferably,  $5\times10^{-6}$  to  $5\times10^{-3}$  mols/m².

To the silver halide photographic light-sensitive materials containing the silver halide emulsions of the invention, a variety of photographic additives besides the above-given compounds may also be added.

Such additives include, for example, a UV absorbent, 10 a development accelerator, a surfactant, a water-soluble antiirradiation dye, a physical surface property improver, a color-contamination inhibitor, a dye-image stabilizer, a water-soluble or oil-soluble fluorescent whitening agent, and a background-color controller.

Among the dye-forming couplers, colored couplers, DIR couplers, DIR compounds, image stabilizers, anticolor-foggants, UV absorbents and fluorescent whitening agents, each of which is other than the cyan couplers relating to the invention and is not necessary to 20 adsorb to the surfaces of silver halide crystals, the hydrophobic compounds may be treated in a variety of dispersing methods such as a solid-dispersing method, a latex-dispersing method, and an oil drops-in-water type emulsifying-dispersing method. The above-given meth- 25 ods may suitably be selected to meet the chemical structures of such hydrophobic compounds such as the above-mentioned couplers. Various types of the oil drops-in-water type emulsifying-dispersing methods may be used for dispersing the hydrophobic compounds 30 such as the couplers, wherein, a hydrophobic compound is normally dissolved in a high boiling organic solvent having a boiling point of about 150° C. and, if required, in making a combination use of a low boiling organic solvent and/or a water-soluble organic sol- 35 vents; the resulting solution is so dispersed as to be emulsified with a surfactant in a hydrophilic binder such as a gelatin solution by making use of a dispersing means such as a stirrer, a homogenizer, a colloid mill, a flowjet mixer or a supersonic apparatus; and, after the dis- 40 persion-emulsification is completed, the resulting emulsion is added into an objective hydrophilic colloidal layer. It is permitted that the above-mentioned process may supplement with a processing step of removing the low boiling organic solvent after or at the same time of 45 the dispersion.

In the invention, the color developing agents applicable to color developers include those having been well-known and widely used in various photographic processes. These developing magnets include, typically, an 50 aminophenol type derivative and a p-phenylenediamine type derivative. These compounds are generally used in the form of salts such as a hydrochloride or a sulfate. These compounds are used in a concentration within the range of, normally, about 0.1 g to about 30 g and, 55 preferably, about 1 g to about 15 g, each per liter of a color developer used.

The aminophenol type developing agents include, for example, o-aminophenol, p-aminophenol, 5-amino-2-hydroxytoluene, 2-amino-3-hydroxytoluene and 2-60 hydroxy-3-amino-1,4-dimethylbenzene.

The particularly useful primary aromatic amine type color developing agents include, for example, an N,N-dialkyl-p-phenylenediamine type compound, and the alkyl and phenyl groups thereof may be substituted with 65 any substituent. The particularly useful compounds among them include, for example, an N,N-diethyl-p-phenylenediamine hydrochloride, an N-methyl -p-

phenylenediamine hydrochloride, an N.N-dimethyl-p-phenylenediamine hydrochloride, a 2-amino-5-(N-ethyl-N-dodecylamino)toluene, an N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, an N-ethyl-N-β-hydroxyethylaminoaniline, a 4-amino-3-methyl-N.N-diethylaniline, and a 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulfonate.

The color developers applicable to process the silver halide photographic light-sensitive materials of the invention may be added with the compounds having been known as the components of the conventional developers, as well as the above-mentioned primary aromatic amine type color developing agents. For example, it is also allowed to add any one of alkalizers such as sodium hydroxide, sodium carbonate and potassium carbonate, an alkali metal thiocyanate, an alkali metal bisulfite, an alkali metal thiocyanate, an alkali metal halide, benzyl alcohol, a water softener and a thickener.

The photographic light-sensitive materials of the invention are preferably processed with a color developer either not containing any water-soluble bromide at all or containing a very few water-soluble bromides. When containing an excess water-soluble bromides, there may be some instances where the developing speed of a photographic light sensitive material may rapidly be lowered. In a color developer, the bromide ion concentration in terms of potassium bromide is about not more than 0.1 g and, preferably, not more than 0.05 g, each per liter of the color developer used.

When using a water-soluble chloride as a development controller in the above-mentioned color developer, the effects of the invention can particularly become remarkable. The water-soluble chlorides may be used in an amount within the range of 0.5 to 5 g and, preferably, 1 g to 3 g, in terms of the potassium chloride content, each per liter of the color developer used.

The pH values of the color developers are, normally, not less than 7 and, most generally, within the range of about 10 to about 13.

The color developing temperatures are, normally, not lower than 15° C. and, generally, within the range of 20° C. to 50° C. For a rapid processing, it is preferable to carry out the process at a temperature of not lower than 30° C. The color development is preferably be carried out for a period of time within the range of 20 seconds to 60 seconds and, more preferably, 30 seconds to 50 seconds.

The silver halide photographic light-sensitive materials relating to the invention can also be processed in an alkaline activation bath, when the hydrophilic colloidal layers thereof contain the above-mentioned color developing agents capable of functioning either as their own or as the precursors thereof. The color developing agent precursors are the compounds capable of producing color developing agents under the alkaline conditions. They include, for example, a Schiff's base type precursor produced with an aromatic aldehyde derivative, a polyvalent metal ion complex precursor, a phthalimide derivative precursor, a phosphoric acid amide derivative precursor, a sugar-amine reactant precursor, and a urethane precursor. These precursors of the aromatic primary amine color developing agents are detailed in, for example, U.S. Pat. Nos. 3,342,599, 2,507,114, 2,695,234 and 3,719,492; British Patent No. 803,783; Japanese Patent O.P.I Publication Nos. 53-185628/1978 and 54-79035/1979; and Research Disclosure, Nos. 15159, 12146 and 13924. The above-men-

tioned aromatic primary amine color developing agents or the precursors thereof should be added in an amount so sufficient as to develop a satisfactory color when an activation process is carried out. The amounts thereof to be added are considerably varied according to the 5 kinds of light-sensitive materials to be processed. However, they are added in an amount within the range of, generally, 0.1 mols to 5 mols and, preferably, 0.5 mols to 3 mols, each per mol of silver halides used. The color developing agents or the precursors thereof may be 10 used independently or in combination. In order to incorporate them into a light-sensitive material, they may be added thereinto after dissolving them in a suitable solvent such as water, methanol, ethanol or acetone. The may also be added thereinto in the form of an emul- 15 sified dispersion thereof prepared with a high boiling organic solvent such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate. Further, they may be added thereinto after impregnating them into a latex polymer, as described in Research Disclosure, No. 20 **1**4850.

After the silver halide photographic light-sensitive materials of the invention are color developed, they are processed in a bleaching step and a fixing step, successively. The bleaching and fixing steps may be carried 25 out at the same time. As for the bleachers, a variety of compounds may be used. Among them, polyvalent metal compounds such as those of iron (III), cobalt (III) and copper (II) and, particularly, the complex salts of these polyvalent metal cations and organic acids may 30 suitably be used independently or in combination, They include, for example, aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid and N-hydroxyethyl ethylenediaminediacetic acid, metal complex salts of malonic acid, tartaric acid, malic 35 acid, diglycolic acid and dithioglycolic acid, or ferricyanic acid salts and dichromates, which may be used independently or in combination.

As for the fixers, soluble complexing agents for making a silver halide soluble to be a complex salt may be 40 used. They include, for example, sodium thiosulfate, ammonium thiosulfate, potassium thiocyanate, thiourea and thioether.

After completing a fixing step, a washing step is usually carried out.

The washing step may be replaced by a stabilizing step, or these two steps may be carried out in combination. The stabilizers used in the stabilizing step may contain a pH buffer, a chelating agent and an antimold. The typical requirements for them may be referred to 50 Japanese Patent O.P.I. Publication No. 58-134636/1983.

# **EXAMPLES**

The invention will be detailed with reference to the following examples. It is, however, to be understood 55 that the embodiments of the invention shall not be limited thereto.

# Example 1

A solution was prepared by adding 60 g of magenta 60 coupler M-1, 40 g of dye-image stabilizer ST-3, 15 g of ST-4 and 1.7 g of antistaining agent HQ-1 into a mixture of 40 ml of high boiling organic solvent DBP and 100 ml of ethyl acetate. The resulting solution was added into an aqueous 5% gelatin solution containing 5 g of 65 sodium dodecylbenzenesulfonate, and the mixture was dispersed by a supersonic homogenizer. The resulting dispersion was finished to make 1500 ml. The dispersion

was added into 1000 ml of an aqueous 3% gelatin solution for coating use and, further, 400 g of a green-sensitive silver chlorobromide emulsion was added thereinto, so that a green-sensitive emulsion layer coating solution was prepared and was then coated on a polyethylene-laminated paper support in order from the support so that the layer arrangements could be as shown in Table-1.

TABLE 1

Layer	Composition	Amount added g/m ²
	Gelatin	1.0
Layer 7	Ociatin	1.0
Protective layer	Gelatin	0.6
Layer 6	UV absorbent UV-1	0.0
UV absorbing	UV absorbent UV-2	0.2
layer		0.2
	Antistaining agent HQ-1	0.01
	DBP PVP	0.2
		0.03
T	Antiirradiation dye AI-2	1.40
Layer 5	Gelatin	0.24
Red-sensitive	Red-sensitive silver	0.24
layer	chlorobromide emulsion.	
	in terms of silver content	0.17
	Cyan coupler C-1	0.17
	Cyan coupler C-2	0.25
	Dye-image stabilizer ST-1	0.2
	High boiling organic solvent HB-1	0.10
	Antistaining agent HQ-1	0.01
	DBP	0.30
Layer 4	Gelatin	1.30
UV absorbing	UV absorbent UV-1	0.40
layer	UV absorbent UV-2	0.40
	Antistaining agent HQ-1	0.03
ı	DBP	0.40
Layer 3	Gelatin	1.40
Green-sensitive	Green-sensitive silver	0.27
layer	chlorobromide emulsion,	
14,41	in terms of silver content	
	Magenta coupler M-1	0.35
	Dye-image stabilizer ST-3	0.23
	Dye-image stabilizer ST-4	0.09
	Antistaining agent HQ-1	0.01
	DBP	0.30
	Antiirradiation dye AI-1	0.01
Layer 2	Gelatin	1.20
Interlayer	Antistaining agent HQ-1	0.12
Interrayer	DBP	0.15
Layer 1	Gelatin	1.30
Blue-sensitive	Blue-sensitive silver	0.30
layer	chlorobromide emulsion,	. 0.50
14 y C1	in terms of silver content	
	Yellow coupler Y-1	0.80
	Dye-image stabilizer ST-1	0.30
	Dye-image stabilizer ST-2	0.30
	Antistaining agent HQ-1	0.20
	DBP	0.02
Support	Polyethylene-laminated paper	

Y-1

M-1

HQ-1

 $(t)C_8H_{17}$ 

**ST-3** 

(t)C₄H₉

ST-4

AÏ-1

35 KO₃S

AI-2

45 KO₃S

HB-1

50 C₁₂H₂₅-

NC-

HOOC-

(t)C₄H₉

20

30

40

OH

OH

OC₄H₉

OC₄H₉

OH

CH₃

# TABLE 1-continued

 $C_8H_{17}(t)$ 

C₄H₉(t)

 $-CH_2-$ 

=CH-CH=CH $\cdot$ 

SO₃K

 $SO_3K$ 

-NHSO₂-

The following H-1 was also used as a hardener.

OH

CH3

HO

KO₃S

=CH-CH=CH-CH=CH-

C₄H₉(t)

HO'

KO₃S

-CH₃

-COOH

 $SO_3K$ 

SO₃K

DBP, dibutyl phthalate

UV-1

The resulting coated sample was named Sample 1.

Then, Samples 2 through 13 were prepared in the same manner as in Sample 1, except that magenta coupler M-1 of Layer 3, the UV absorbents of Layers 4 and 6, the whole amount of gelatin added, and the combinations of the silver halide emulsions and the processing

15

35

50

65

steps of Sample 1 were each changed as shown in Table

The Samples 1 through 13 were each exposed to light and were then processed in the following processing steps:

Processing Step A	Temperature	Time
Color developing	32.8° C.	3 min. 30 sec.
Bleach-fixing	32.8° C.	1 min. 30 sec.
Washing	32.8° C.	3 min. 30 sec.
Color developer		-
N-ethyl-N-β-methanesulfor	amidoethyl-	4.0 g
3-methyl-4-aminoaniline sul	lfate	
Hydroxylamine sulfate		2.0 g
Potassium carbonate		25.0 g
Sodium chloride		0.1 g
Sodium bromide		0.2 g
Sodium sulfite anhydride		2.0 g 10.0 ml
Benzyl alcohol Polyethylene glycol,		3.0 ml
with an average polymeriza	ation degree: 400	<b>210</b> 1111
Add water to make in total	_	1 liter
Adjust pH with sodium hy		pH 10.0
Bleach-fixer		-
Iron(III) sodium ethylenedi	iaminetetraacetate	60.0 g
Sodium thiosulfate		100.0 g
Sodium bisulfite		20.0 g
Sodium metabisulfite		5.0 g
Add water to make		1 liter
Adjust pH to be	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	pH 7.0
Processing step B	Temperature	Time
Color developing	$35.0 \pm 0.3^{\circ} C$ .	45 sec.
Bleach-fixing	$35.0 \pm 0.5^{\circ} C.$	45 sec.
Stabilizing	30 to 34° C.	90 sec.
Drying	60 to 80° C.	60 sec.
Color developer		
Pure water		800 ml
Triethanolamine		10 g
N,N-diethylhydroxylamine Potassium bromide		5 g 0.02 g
Potassium chloride		2 g
Potassium sulfite		0.3 g
1-hydroxyethylidene-1,1-dip	phosphoric acid	1.0 g
Ethylenediaminetetraacetic	•	1.0 g
Disodium catechol-3,5-disu	lfonate	1.0 g
N-ethyl-N- $eta$ -methanesulfon	amidoethyl-	4.5 g
3-methyl-4-aminoaniline sul		
Fluorescent whitening ager		1.0 g
4,4'-diaminostilbenedisulfon	ic acid derivative	27 -
Potassium carbonate Add water to make in total	of	27 g 1 liter
Adjust pH to be	. 01	pH = 10.10
Bleach-fixer		p11 10.10
Ferric ammonium ethylene	diamine-	60 g
tetraacetate, dihydrate		
Ethylenediaminetetraacetic	acid	3 g
Ammonium thiosulfate.		100 ml
in an aqueous 70% solution	1	
Ammonium sulfite,		27.5 ml
in an aqueous 40% solution		<b>a</b> ••.
Add water to make in total		l liter
Adjust pH with potassium a	carbonate or	pH = 5.7
glacial acetic acid to be Stabilizer		
5-chloro-2-methyl-4-isothia:	zoline-3-one	1.0 g
Ethylene glycol		1.0 g
1-hydroxyethylidene-1,1-dip	phosphoric acid	2.0 g
Ethylenediaminetetraacetic	acid	1.0 g
Ammonium hydroxide, in a	in aqueous 20%	3.0 g
•	_	-

-continued	
•COMMULEU	
<b>~</b> • • • • • • • • • • • • • • • • • • •	

3.0 g
1.5 g
1 liter
pH = 7.0

After the samples were processed, the following evaluations were carried out. The results thereof are shown in Table-2.

#### Sweating phenomena

After the processed samples were stored for four weeks under the conditions of 80° C. and 60% RH, the amounts of oily matters produced on the surfaces of the samples were taken and measured. The visual judgements were also tried.

- O... No sweat was found at all.
- $\Delta$  . . . Slight sweats were found.
- X... Serious sweats found and the surfaces were found to be sticky.

# White background

After the samples were processed, they were stored for one week under the conditions of 80° C. and 60% RH, the difference of the blue color densities, ΔDa, was measured between the unexposed portions thereof before and after the storage.

#### Pressure resistance

Before exposing the samples to light, the emulsion surfaces of the samples were scratched by a Heidon scratch hardness tester, Model 18, manufactured by 40 Shintoh Science Company, while applying the surfaces of the samples with the loads of 5, 10, 20, 30 and 50 g, respectively. After the samples were exposed to light and processed in the same manner as in the aforementioned manner, the sensitization and desensitization produced thereby were evaluated in terms of the following five grades:

 o... Excellent, 
 o... Good, 
 o... Slightly produced, 
 duced, 
 X... Produced, and 
 X... Seriously produced

# Tone

A color chart manufactured by Macbeth Company was photographed on a 'Konica Color GX-II 100' color negative film manufactured by Konica Corporation, and was then processed. Using the resulting negative film and adjusting the tones in the grey scale portions, each of the samples was exposed to light through the negative film and was then processed. The resulting prints were evaluated on the color reproducibilities of the hues produced thereon.

- (a) . . . Both of the chroma and color reproduction fidelity were found to be high,
- O... The color reproduction fidelity was found to be high, and
- $\Delta \dots A$  chromatic aberration was found in hues.

TABLE 2

			Total amount of			_	Sw	eat	Pres-		Color	•
Sample No.	Magenta coupler	UV absorb- ent	gelatin added. g/m ²	AgX. Br mol %	Process- ing step	White back- ground	mg/ cm²	Visual evalu- ation	sure resist- ance	Red	Pur- ple	tion Blue
1, Comp. 2, Comp. 3, Comp. 4, Comp. 5, Comp. 6, Inv. 7, Inv. 8, Inv. 9, Inv. 10, Inv. 11, Comp. 12, Inv.	M-1 10, Exemp. 10, Exemp. 10, Exemp. 10, Exemp. 14, Exemp. 23, Exemp. 23, Exemp. 23, Exemp. 10, Exemp. 10, Exemp.	UV-1/-2 UV-18L UV-18L UV-6L UV-13L UV-1/-2	<ul> <li>8.2</li> <li>7.6</li> <li>8.2</li> <li>7.6</li> </ul>	80 80 80 80 80 80 80 80 80 0.5	A A A A A A A B B	0.42 0.40 0.23 0.22 0.18 0.19 0.16 0.16 0.17 0.24 0.17 0.16	0.05 0.06 0.05 0.03 0.03 0.02 0.02 0.06 0.02	2 x x x x x x x 0000 x 0	OA A X OOOOX O	44000040	400000000	400000000

Comp.: Comparative Inv.: Inventive Exemp.: Exemplified

As can be understood from Table-2, in Samples 1 and 2 applied with the comparative couplers thereinto, the tones thereof were deteriorated and any improvement of the white background thereof could not be found at 25 all and, besides, there were also serious deteriorations in sweating phenomena.

On the other hand, in Sample 3 applied with the combination of the couplers of the invention and the conventional UV absorbents thereinto, the improvements of the tones thereof were found, however, the tones were found to be slightly contaminated through

2 in a proportion of 1:1, the same effects of the invention could also be obtained, respectively.

# Example 3

Sample 14 was prepared in the same manner as in Example except that, in Layer 4 of Sample 13 prepared in Example 1, the amount of the antistaining agent added therein was replaced by 0.11 g/m². The resulting Sample 14 was processed and evaluated in the same manner as in Example 1. The results thereof are shown in Table-3.

TABLE 3

		<b></b>	<u> </u>	<u> </u>			
		Swe	at		re	Color product	ion
Sample No.	White background	mg/cm ²	Visual test	Pressure resistance	Red	Pur- ple	Blue
11 comp. 13 Inv. 14 Inv.	0.24 0.16 0.15	0.06 0.01 0.01	<b>X</b>	<b>XX</b> ○ ⊙	<b>∆</b> ○⊚	000	000

the visual observations, and the pressure resistance was seriously deteriorated. In the Samples 4 and 5, an improvement could hardly be found out. However, in Sample 6 of the invention, there were not any deteriorations in sweating phenomena, but the improvement effects on the white background and pressure resistance and, in addition, there were the remarkable effects on the color reproducibility. The above-mentioned effects could not ever foresee at all from the conventional 50 knowledge.

From the coupler, Exemplified Compound 23 used in Sample 8, the more excellent results were obtained.

In addition to the above, in Samples 11 through 13 each using a high silver chloride-containing emulsion in 55 the above-mentioned system, they were proved to be useful, because the effects of the invention could further be emphasized.

# Example 2

When the magenta coupler, Exemplified Compound 10, of Samples 6 and 12 in Example 1 was replaced by Exemplified-compounds 9, 22, 24, 26, 41, 46 and 50, respectively, the same effects of the invention could also be obtained.

When the UV absorbents were replaced by UV-8L, Uv-1IL, UV-15L, a mixture of UV-18L/UV-1 in a proportion of 1:1, and another mixture of UV-18L/UV-

As is obvious from Table-3, Sample 14 could display the effects of the invention more than others.

# Sample 4

Onto a paper support laminated with polyethylene on one side thereof and titanium oxide-containing polyethylene on the other side thereof, each of the layers having the compositions shown in Table-4 was coated respectively, thereby preparing a multilayered silver halide color photographic light-sensitive material. In the table, the amounts of the compositions added are shown in terms of  $g/m^2$  and the amounts of the silver halide emulsions are shown in terms of the silver contents.

TABLE 4

<b>6</b> 0	Layer	Composition	Amount added g/m ²
	Layer 7	Gelatin	1.00
	Protective layer	SiO ₂ having an average particle-size of 3 µm	0.003
	Layer 6	Gelatin	See Table-5
65	UV absorbing	UV absorbent, See Table-5	See Table-5
UJ	layer	Color mixing inhibitant HQ-2	0.001
		High boiling solvent DNP PVP	See Table-5 0.03
	Layer 5	Red-sensitive silver chlorobromide	0.24

TABLE 4-continued

		_		_	_
TA	TT	Г	4-con	. 4	
14	KI	<b>.</b> —	4-con	1	户门

Layer	Composition	Amount added g/m ²		Layer	Composition	Amount added g/m ²
Red-sensitive	emulsion spectrally sensitized with	· · · · · · · · · · · · · · · · · · ·	5		High boiling solvent DOP	0.25
layer	sensitizing dye D-1, containing			Layer 2	Gelatin	1.20
<b>-</b>	silver bromide of 80 mol %			Interlayer	Color mixing inhibitant HQ-3	0.04
	Gelatin	1.20		•	High boiling solvent DIDP	0.10
	Cyan coupler C-2	0.40		Layer 1	Blue-sensitive silver chloro-	0.30
	Dye-image stabilizer ST-1	0.22		Blue-sensitive	bromide emulsion spectrally	
	High boiling solvent DOP	0.22	10	layer	sensitized with sensitizing dye	
Layer 4	Gelatin	See Table-5			D-3, having a silver bromide	
UV absorbing	UV absorbent, See Table-5	See Table-5			content of 80 mol %	
layer	Color mixing inhibitant HQ-2	0.03			Gelatin	1.20
	High boiling solvent DNP	See Table-5			Yellow coupler, See Table-5	0.80
Layer 3	Green-sensitive silver chloro-	0.20			Dye-image stabilizer ST-1	0.30
Green-sensitive	bromide emulsion spectrally		15		Dye-image stabilizer ST-2	0.15
layer	sensitized with sensitizing dye				High boiling solvent DNP	0.30
•	D-2, having a silver bromide	•		Support	Polyethylene-laminated paper	
	content of 80 mol %					
	Gelatin	1.40		A - C 41	tito-to-to-to-to-to-to-to-to-to-to-to-	S 1 and hand
	Magenta coupler M-2	0.38			coating assistants, surfactant	5-1 and naru
	Dye-image stabilizer ST-5	0.10	20	ener H-1 we		
	Dye-image stabilizer ST-6	0.10		Besides th	e above, antiirradiation dyes A	I-1, AI-3 and
	Dye-image stabilizer ST-7	0.10		AI-4 were a	•	•

$$\begin{array}{c} CH_{3} \\ CH_{2} \\ CH_{2$$

ST-5

**S-1** 

-continued

$$CH_3$$
  $CH_3$ 
 $CH_3$ 
 $CH_{11}(t)$ 
 $C_4H_9(t)$ 
 $C_4H_9(t)$ 
 $CH_3$ 
 $C_5H_{11}(t)$ 
 $C_4H_9(t)$ 

$$\begin{array}{c} OC_4H_9(t) \\ \\ C_4H_9(t) \\ \\ OC_4H_9(t) \end{array}$$
 ST-6

$$O_2S$$
 $N$ 
 $O_6H_{13}$ 

DOP: Dioctyl phthalate

DNP: Dinonyl phthalate

DIDP: Diisodecyl phthalate

SO₃K

CH₃

$$C_{12}H_{25}$$
 $C_{12}H_{25}$ 
 $C_{12}H_{25}$ 
 $C_{13}H_{25}$ 
 $C_{13}H_{25}$ 
 $C_{14}H_{25}$ 
 $C_{15}H_{25}$ 
 $C_{1$ 

 $SO_3K$ 

TABLE 5

	•							
	Layer 1		Layer 4			Layer 6		
Sample No.	Yellow coupler	UV absorbent	Amount of DNP	Amount of gelatin	UV absorbent	Amount of DNP	Amount of gelatin	Total amount of gelatin
1 Comp.	<b>Y-1</b>	UV-4S 0.60	0.40	1.1	UV-4S 0.40	0.25	0.6	7.7
2 Comp.	XI-3	UV-4S 0.60	0.40	1.1	UV-4S 0.40	0.25	0.6	7.7
3 Comp.	Y-1	UV-4S 0.60	0.40	0.9	UV-4S 0.40	0.25	0.5	7.4
4 Comp.	XI-3	UV-4S 0.60	0.40	1.6	UV-4S 0.40	0.25	1.0	8.6
5 Comp.	Y-1	UV-18L 0.60	0	1.1	UV-18L 0.40	0	Ò.6	7.7
6 Comp.	XI-3	UV-4S 0.60	0.40	0.9	UV-4S 0.40	0.25	0.5	7.4
7 Comp.	Y-1	UV-18L 0.60	0	0.9	UV-18L 0.40	0	0.5	7.4
8 Comp.	XI-3	UV-18L 0.60	0	1.1	UV-18L 0.40	0	0.6	7.7
9 Inv.	XI-3	UV-18L 0.60	0	0.9	UV-18L 0.40	. 0	0.5	7.4
10 Inv.	XI-3	UV-18L	0	0.9	UV-18L	0	0.5	7.4

40

50

55

60

TABLE 5-continued

	Layer 1	·	Layer 4	· · · · · · · · · · · · · · · · · · ·		Layer 6		_
Sample No.	Yellow coupler	UV	Amount of DNP	Amount of gelatin	UV _absorbent	Amount of DNP	Amount of gelatin	Total amount of gelatin
		0.40 UV-4S 0.20			0.30 UV-4S 0.10			
II Inv.	XI-3	UV-18L 0.60	0	0.6	UV-18L 0.40	0	0.3	6.9
12 Inv.	XI-18	UV-14L 0.60	0	0.9	UV-14L 0.40	0	0.5	7.4
13 Inv.	X1-3	UV-10L 0.40 UV-7S 0.20	0.20	0.9	UV-10L 0.30 UV-7S 0.10	0.10	0.5	7.4

#### Comparative coupler Y-1

(CH₃)₃CCOCHCONH—
ONHCO(CH₂)₃O—
$$C_5H_{11}(t)$$

NHCO(CH₂)₃O
 $C_5H_{11}(t)$ 

The resulting sample was exposed to light in an ordinary method and was then processed in the following processing steps.

Processing step A	Temperature	Time
Color developing	33° C.	3 min. 30 sec
Bleach-fixing	33° C.	1 min. 30 sec
Washing	33° C.	3 min.
Drying	70° C.	1 min.
Color developer		· · · · · · · · · · · · · · · · · · ·
N-ethyl-N-β-methanesulfor	namidoethyl-	4.9 g
3-methyl-4-aminoaniline su		_
Hydroxylamine sulfate		2.0 g
Potassium carbonate		25.0 g
Sodium bromide		0.6 g
Sodium sulfite anhydride		2.0 g
Benzyl alcohol		13 ml
Polyethylene glycol, havin	g an average	3.0 ml
polymerization degree of 4	00	
Add water to make		1 liter
Adjust pH with sodium hy	droxide to be	pH = 10.0
Bleach-fixer		
Ferric sodium ethylenedian	ninetetraacetate	60 g
Ammonium thiosulfate		100 g
Sodium bisulfite		10 g
Sodium metabisulfite		3 g
Add water to make		1 liter
Adjust pH with aqueous as	mmonia to be	pH = 7.0

The processed samples were subjected to the evaluation tests in the following manner. The results thereof are shown in Table-6.

# Color reproducibility

A color chart was photographed on a 'Konica Color GX-II 100' color negative film manufactured by Konica Corporation, and was then processed. Using the pro- 65 cessed film, the prints of the color chart were made on each of the samples and the color reproducibility thereof were evaluated.

# Sweating property

After the samples were stored in a test chamber under the conditions of 85° C. and 60% RH for 21 days, the degrees of sweats produced on the surfaces of the samples were evaluated.

# Curling property

After the samples were stored in a test chamber under the conditions of 23° C. and 20% RH for 24 hours, the degrees of curlings produced on the samples were evaluated.

TABLE 6

Sample		Color reproduc			** *** Sweating Curlin		
No.	Yellow	Magenta	Cyan	Total	property	property	
1 Comp.	2	4	4	2	$\circ$	X	
2 Comp.	4	4	4	4	$\widecheck{\Delta}$	X	
3 Comp.	2	4	4	2	$\Delta$	$\circ$	
4 Comp.	4	3	3	3	$\bigcirc$	XX	
5 Comp.	2	4	4	2	Ŏ	X	
6 Comp.	4	4	4	4	$\check{\mathbf{X}}$	$\circ$	
7 Comp.	2	4	4	2	$\Delta$	Ŏ	
8 Comp.	4	4	4	4	$\bigcirc$	$\widecheck{\mathbf{X}}$	
9 Comp.	5	4	4	5	Ŏ	$\bigcirc$	
10 Inv.	5	4	4	5	Ŏ	Ŏ	
11 Inv.	5	4	4	5	Ŏ	$\widetilde{\mathfrak{O}}$	
12 Inv.	5	5	5	5	Ŏ	$\tilde{C}$	

TABL	$\mathbf{F}$	antinu.	ച
TADL	E U-C	ommu	ZU

Sample		Color reproduc			** Sweating		
No.	Yellow	Magenta	Cyan	Total	property	property	
13 Inv.	5	4	4	5		0	
*Color reproducts  5 = Excelle  4 = Good  3 = Accepta  2 = Poor  1 = Very Parity  **Sweating  O = No swart  A = Some some some some some some some some s	able  oor  property: eat product weats product seriously property: ent	ed luced					

As is obvious from Table-6, when making the combination use of the yellow coupler of the invention and a liquid UV absorbent, the sweating property improvements could be synergistically achieved. Further, the improvements of the color reproducibility and curling property could also be achieved. As an advantage of reducing the amounts of gelatin used, not only the curling property improvements but also the color reproducibility improvements could also be achieved in the whole.

#### Example 5

A sample was prepared in the same manner as in Example 4, except that the silver halide emulsion used in Example 4 was replaced by a silver chlorobromide emulsion having a silver chloride content of 99.5 mol %. The resulting sample was evaluated upon exposing it 35 to light and then processing it as in Example 4.

The sample was processed in the following processing steps.

Processing step B	Temperature	Time
Color developing	35° C.	45 sec.
Bleach-fixing	35° C.	45 sec.
Stabilizing	33° C.	90 sec.
Drying	70° C.	60 sec.
Color developer		•
Pure water		800 ml
Triethanolamine		10 g
N,N-diethylhydroxylamine	<b>?</b>	5 g
Potassium bromide		0.02 g
Potassium chloride		2 g
Potassium sulfite		0.3 g
1-hydroxyethylidene-1,1-d	iphosphoric acid	1.0 g
Ethylenediaminetetraacetic	c acid	1.0 g
Disodium catechol-3,5-dist		1.0 g
N-ethyl-N-β-methanesulfo	namidoethyl-	4.5 g
3-methyl-4-aminoaniline su		
Fluorescent whitening age		1.0 g
4,4'-diaminostilbenedisulfo	nic	
acid derivative		
Potassium carbonate		27 g
Add water to make in total		1 liter
Adjust pH with potassium	hydroxide or	pH = 10.10
sulfuric acid to be		
Bleach-fixer	-	
Ferric ammonium ethylen	ediamine-	60 g
tetraacetate dihydrate		
Ethylenediaminetetraaceti	c acid	3 g
Ammonium thiosulfate,		100 ml
in an aqueous 70% solutio	n	
Ammonium sulfite,		27.5 ml
in an aqueous 40% solutio	n	
Add water to make		1 liter
Adjust pH with potassium	carbonate or	pH = 6.2
<del>-</del>		

	-continued		•
	glacial acetic acid to be Stabilizer	-	
	5-chloro-2-methyl-4-isothiazoline-3-one	1.0 g	
•	Ethylene glycol	1.0 g	
	1-hydroxyethylidene-1.1-diphosphonic acid	2.0 g	
	Ethylenediaminetetraacetic acid	1.0 g	
	Ammonium hydroxide.	3.0 g	
	in an aqueous 20% solution		
ገ	Ammonium sulfite	3.0 g	
,	Fluorescent whitening agent,	1.5 g	
	4,4'-diaminostilbenedisulfonic acid		•
	derivative		
	Add water to make	1 liter	
	Adjust pH with sulfuric acid or	pH = 7.0	

The results of the evaluations were the same as in Example 4.

potassium hydroxide to be

In the combination of processing step B not containing any benzyl alcohol and the invention, the color reproducibility was further improved.

# Example 6

On a paper support laminated with polyethylene on one side thereof and with polyethylene containing titanium oxide on the other side thereof which is on the side of Layer 1, each of the layers having the compositions shown in Table-7 was coated, so that a multilayered silver halide color photographic light-sensitive material was prepared. The coating solutions therefor were prepared in the following manners.

# Layer 1 coating solution

Ethyl acetate was added in an amount of 60 ml into a mixture of 26.7 g of yellow coupler Y-1, 0.67 g of antistaining agent HQ-1, 10 g of dye-image stabilizer ST-2 and 8.5 g of high boiling organic solvent DBP, and dissolved together. The resulting solution was dispersed emulsion-wise into 300 ml of an aqueous 10% gelatin solution containing 15 ml of an aqueous 10% sodium alkylnaphthalenesulfonate solution by making use of a homogenizer, thereby preparing a yellow coupler dispersion.

The resulting dispersion was mixed up with a blue-sensitive silver chlorobromide emulsion containing silver chloride of 10 mol % and silver bromide of 90 mol % and a gelatin coating solution, thereby preparing Layer 1 coating solution.

# Layer 3 coating solution

High boiling organic solvent DBP was added in an amount of 24 g into a mixture of 30 g of magenta coupler M-1, 20 g of dye-image stabilizer ST-4, 7.5 g of dye-image stabilizer ST-3 and 0.85 g of antistaining agent HQ-4, and 50 ml of ethyl acetate was further added thereinto to be dissolved together. The resulting solution was dispersed emulsionwise into 400 ml of an aqueous 5% gelatin solution containing 25 ml of an aqueous 10% sodium dodecylbenzenesulfonate solution by making use of a homogenizer, thereby preparing a magenta coupler dispersed solution.

The resulting solution was mixed up with a blue-sensitive silver chlorobromide emulsion containing silver chloride of 20 mol % and silver bromide of 80 mol % and a gelatin coating solution, thereby preparing Layer 3 coating solution.

# Layer 5 coating solution

To a mixture of 7 g of cyan coupler C-1, 10 g of cyan coupler C-2, 8 g of dye-image stabilizer ST-1, 0.4 g of antistaining agent HQ-4 and 8 g of high boiling organic solvent HB-2, 40 ml of ethyl acetate was added. The resulting solution was dispersed emulsionwise in an aqueous 10% gelatin solution containing 10 ml of a 10% sodium alkylnaphthalenesulfonate solution by making use of a homogenizer, thereby preparing a cyan coupler dispersing solution.

The resulting dispersed solution was mixed up with a red-sensitive silver chlorobromide emulsion containing silver chloride of 30 mol % and silver bromide of 70 mol % and a gelatin solution for coating use, thereby preparing Layer 5 coating solution.

The coating solutions each for Layers 2, 4, 6 and 7 were also prepared in the same manner as in the above-described Layer 1 coating solution, as shown in Table-20 7. As for the gelatin hardener, the following compound H-1 was also added to each of the solutions.

TABLE 7

Layer	Composition	Amount added g/m ²
Layer 7	Gelatin	0.9
Protective	Ociatin	0.7
layer	Calasin	0.5
Layer 6	Gelatin UV absorbent UV-1	0.3
UV absorbing	UV absorbent UV-2	0.2
layer		0.2
	Antistaining agent HQ-4 DBP	0.01
	PVP	0.03
		0.03
I aver 5	Antiirradiation dye AI-5 Gelatin	1.30
Layer 5	Red-sensitive silver chloro-	0.24
Red-sensitive		U.2 <del>4</del>
layer	bromide emulsion, containing Cl 30%, Br 70%, in terms of silver	
	content:	0.10
	Cyan coupler C-1	0.18
	Cyan coupler C-2	0.25
	Dye-image stabilizer ST-1	0.20
	High boiling organic solvent HB-2	0.20
	Antistaining agent HQ-4	0.01
Layer 4	Gelatin	1.10
UV absorbing	UV absorbent UV-1	0.40
layer	UV absorbent UV-2	0.40
	Antistaining agent HQ-4	0.03
	DBP	0.40
Layer 3	Gelatin	1.40
Green-sensitive	Green-sensitive silver chloro-	0.27
layer	bromide emulsion containing Cl 20%, Br 80%, in terms of silver	
	content:	0.25
	Magenta coupler M-1	0.35
•	Dye-image stabilizer ST-4	0.23
	Dye-image stabilizer ST-3	0.09
	High boiling organic solvent DBP	0.28
	Antiirradiation dye Al-1	0.01
Layer 2	Gelatin	1.20
Interlayer	Antistaining agent HQ-4	0.12
	DBP	0.15
Layer 1	Gelatin	1.20
Blue-sensitive	Blue-sensitive silver chloro-	0.30
layer	bromide emulsion, containing Cl 10%, Br 90%, in terms of	
	silver content:	
	Yellow coupler Y-1	0.80
	Dye-image stabilizer ST-2	0.30
	Antistaining agent HQ-4	0.02
<b>C</b>	DBP	0.25
Support	Polyethylene-laminated paper	

HQ-4

TABLE 7-continued

Next, Samples 2 through 12 were prepared in the same manner as in Sample 1, except that, in Sample 1, magenta coupler M-1 and the amount of gelatin added, each of Layer 3, and cyan couplers C-1, C-2 and the amount of gelatin added, each of Layer 5, were replaced by those shown in Table-8.

TABLE 8

		Lay	er 3	Lay	er 5
60	Sample No.	Magenta coupler	Gelatin added	Cyan coupler	Gelatin added
	1 Comparative	M-1	1.40	C-1/C-2	1.30
	2 Inventive	M-3	1.40	C-1/C-2	1.30
	3 Inventive	M-4	1.40	C-1/C-2	1.30
	4 Inventive	I-66	1.40	C-1/C-2	1.30
55	5 Inventive	I-66	1.40	XXXI-15	1.30
,,,	6 Inventive	I-66	1.35	XXXI-18	1.30
	7 Comparative	M-1	1.50	C-1	1 40
	8 Inventive	M-3	1.35	C-2	1.30
	9 Inventive	M-4	1.35	C-2	1.30

TABLE 8-continued

	Lay	ег 3	Layer 5		
Sample No.	Magenta coupler	Gelatin added	Cyan coupler	Gelatii added	
10 Inventive	I-24	1.35	C-2	1.30	
11 Inventive	I-24	1.35	XXXI-4	1.30	
12 Inventive	I-24	1.35	XXXI-4/C-2	1.30	

Gelatin amounts are shown in terms of g/m².

The resulting samples were exposed wedgewise to light by making use of a sensitometer, Model KS-7, manufactured by Konica Corporation, and were then processed in the following color developing steps. The evaluations thereof were made as follows.

Processing step Time Temperature

#### Color tone

A color chart, manufactured by Macbeth Company, was photographed on a 'Konica Color GX II 100' color negative film manufactured by Konica Corporation, and the photographed film was then processed. Using the processed negative film and adjusting the tones in the grey scale portions of the film, each sample was exposed to light through the film and processed. The color reproducibility of each sample was visually evaluated on each of the hues of the resulting prints.

- O... Color reproduction had no color stain, close to the original.
- 1/3 ... Color reproduction has a slight color stains.
- X... Color reproduction had color stains.

The results of the evaluations are shown in Table-9.

	T	A	B	L	E	9
--	---	---	---	---	---	---

Sample	Photop	tic color fac	ling. %	Dark	color fadin	g. %	C	olor	tone
No.	Yellow	Magenta	Cyan	Yellow	Magenta	Cyan	В	G	R
1 Comp.	80	80	81	85	81	72	$\mathbf{X}$	Δ	X
2 Inv.	80	47	81	85	89	72	$\bigcirc$	Δ	$\circ$
3 Inv.	80	62	81	85	87	72	$\bigcirc$	Δ	$\circ$
4 Inv.	80	78	81	85	88	72	$\bigcirc$	$\Delta$	$\circ$
5 Inv.	80	78	82	85	86	84	$\bigcirc$	$\bigcirc$	$\circ$
6 Inv.	80	78	81	85	85	83	$\mathcal{O}$	$\bigcirc$	$\circ$
7 Comp.	80	82	85	85	81	43	$\mathbf{X}$	$\circ$	$\mathbf{X}^{\cdot}$
8 Inv.	80	44	79	85	87	94	$\bigcirc$	Δ	$\circ$
9 Inv.	80	57	<b>7</b> 9	85	85	94	$\bigcirc$	Δ	$\circ$
10 Inv.	80	80	79	85	86	94	Õ	Δ	$\circ$
11 Inv.	80	80	82	85	86	84	Ō	$\circ$	$\circ$
12 Inv.	80	80	81	85	86	89	Ŏ	Ŏ	0

33° C. 3 min. 30 sec. Color developing 33° C. 1 min. 30 sec. Bleach-fixing 33° €. 3 min. Washing Color developer formula 4.9 g N-ethyl-N-\beta-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate 2.0 g Hydroxylamine sulfate 25.0 g Potassium carbonate 0.6 gSodium bromide 2.0 g Sodium sulfite anhydride 13 ml Benzyl alcohol 3.0 g Diethylenetriaminepentaacetic acid 10.0 g Triethanolamine 10.0 g Diethylene glycol 1 liter Add water to make pH = 10.0Adjust pH with sodium hydroxide to be Bleach-fixer formula 6.0 g Iron III sodium ethylenediaminetetraacetate 100 g Ammonium thiosulfate 10 g Sodium bisulfite Sodium metabisulfite 1 liter Add water to make pH = 7.0Adjust pH with aqueous ammonia to be

# Photoptic color fading property

The resulting samples were stored outdoors by exposing them to sun rays on an exposure table for one month, and the photoptic color fading properties 60 thereof were evaluated.

# Dark color fading property

The resulting samples were stored under the conditions of 85° C. and 60% RH for 20 days, and the dark 65 color fading properties thereof were evaluated by obtaining the dye-image residual percentages at the initial density of 1.0.

As is obvious from Table-9, in the combination of the couplers in Samples 1 and 7, the color tone was inferior to the others. In Samples 2 through 6 and 8 through 12, such color tones could be improved by using magenta couplers of the invention.

In both of the photoptic and dark color fading properties of Samples 5, 6, 11 and 12, their yellow, magenta and cyan color fading ratios were almost equivalent to each other, and their three-color fading balance were kept excellent.

# Example-7

A multilayered color light-sensitive material was prepared in the same manner as in Example-6 by coating each of the layers having the compositions shown in Table-10 onto a polyethylene-laminated paper support which was the same as that of Example-6. The coating solutions were prepared in the following manner.

# Layer 1 coating solution

A mixture of 27.2 g of yellow coupler Y-2, 0.67 g of antistaining agent HQ-4, 5 g of dye-image stabilizer ST-2, 10 g of dye-image stabilizer ST-1, and 8.5 g of high boiling organic solvent DBP was dissolved in 60 ml of ethyl acetate. The solution resulted was then dispersed emulsionwise, by making use of a homoge-60 nizer, in 300 ml of an aqueous 10% gelatin solution containing 15 ml of an aqueous 10% sodium alkylnaph-thalenesulfonate solution, so that a yellow coupler dispersed solution was prepared.

The resulting dispersed solution was mixed up with a blue-sensitive silver chlorobromide emulsion containing silver chloride of 99.5 mol % and silver bromide of 0.5 mol %, and a gelatin coating solution, so that Layer 1 coating solution was prepared.

Y-2

40

45

# Layer 3 coating solution

A mixture of 30 g of magenta coupler M-1, 20 g of dye-image stabilizer ST-4, 6 g of dye-image stabilizer ST-5, 0.85 g of antistaining agent HQ-4, and 24 g of high 5 boiling organic solvent DBP was dissolved in 50 ml of ethyl acetate. The solution resulted was dispersed emulsionwise, by making use of a homogenizer, in 400 ml of an aqueous 5% gelatin solution containing 25 ml of an aqueous 10% sodium dodecylbenzenesulfonate, so that 10 a magenta coupler dispersed solution was prepared.

The dispersed solution was mixed up with a blue-sensitive silver chlorobromide emulsion containing silver chloride of 99.5% and silver bromide of 0.5%, and a gelating coating solution, so that Layer 3 coating solution was prepared.

# Layer 5 coating solution

A mixture of 7 g of cyan coupler C-1, 10 g of cyan coupler C-2, 8 g of dye-image stabilizer ST-1, 0.4 g of antistaining agent HQ-4, 8 g of high boiling organic solvent HB-2 and 4 g of high boiling organic solvent HB-3 was dissolved in 40 ml of ethyl acetate. The solution resulted was dispersed emulsionwise in 300 ml of an 25 aqueous 10% gelatin solution containing 10 ml of an aqueous 10% sodium alkylnaphthalenesulfonate solution, by making use of a homogenizer, so that a cyan coupler dispersed solution was prepared.

The resulting dispersed solution was mixed up with a 30 red-sensitive silver chlorobromide emulsion containing silver chloride of 99.8 mol % and silver bromide of 0.2 mol % and a gelatin coating solution, so that Layer 5 coating solution was prepared.

The layer coating solutions for Layers 2, 4, 6, and 7 35 layers were each prepared in the same manner as in the above-mentioned Layer 1 coating solution, as shown in Table-10. As for the gelatin hardeners for the solutions, hardener H-1 was added into each of the coating solutions as in Example-6.

TABLE 10

Layer	Composition	Amount added g/m ²
Layer 7 Protective	Gelatin	<b>0</b> .9
layer		
Layer 6	Gelatin	0.5
UV absorbing	UV absorbent UV-1	0.2
layer	UV absorbent UV-2	0.2
	Antistaining agent HQ-4	0.01
	DBP	0.2
	PVP	0.03
	Antiirradiation dye AI-4	0.02
Layer 5	Gelatin	1.30
Red-sensitive	Red-sensitive silver chloro-	0.24
layer	bromide emulsion, containing Cl	
	of 99.8% and Br of 0.2%,	
	in terms of silver content	
	Cyan coupler C-1	0.18
	Cyan coupler C-2	0.25
	Dye-image stabilizer ST-1	0.20
	Antistaining agent HQ-4	0.01
	High boiling organic solvent HB-2	0.20
	High boiling organic solvent HB-3	0.10
Layer 4	Gelatin	1.10
UV absorbing	UV absorbent UV-1	0.40
layer	UV absorbent UV-2	0.40
	Antistaining agent HQ-4	0.03
	DBP	0.40
Layer 3	Gelatin	1.40
Green-sensitive	Green-sensitive silver chloro-	0.27

#### TABLE 10-continued

layer	bromide emulsion, containing Cl	
	of 99.5% and Br of 0.5%.	
	interms of silver content	
	Magenta coupler M-1	0.35
	Dye-image stabilizer ST-4	0.23
	Dye-image stabilizer ST-5	0.07
	High boiling organic solvent DBP	0.28
	Antiirradiation dye AI-1	0.01
Layer 2	Gelatin	1.20
Interlayer	Antistaining agent HQ-4	0.12
•	DBP	0.15
Layer 1	Gelatin	1.20
Blue-sensitive	Blue-sensitive silver chloro-	0.30
layer	bromide emulsion, containing Cl	
	of 99.5% and Br of 0.5%,	
	in terms of silver content	
	Yellow coupler Y-2	0.82
	Dye-image stabilizer ST-2	0.15
	Dye-image stabilizer ST-1	0.30
:	Antistaining agent HQ-4	0.02
	DBP	0.25
Support	Polyethylene-laminated paper	

ST-5  $C_{12}H_{25}-N$  $N-C_{12}H_{25}$ 

HB-3 NHSO₂-C₁₂H₂₅·

The resulting sample was named Sample 2-1. Next, Samples 2-2 through 2-19 were prepared in the same manner as in Sample 2-1, except that magenta coupler M-1 and the amount of gelatin each of Layer 3 and cyan couplers C-1 and C-2 and the amount of gelatin each of Layer 5 were replaced by those shown in Table-11.

TABLE 11

		Lay	er 3	Layer 5		
55 <u>s</u>	Sample No.	Magenta coupler	Gelatin amount	Cyan coupler	Gelatin amount	
2	2-1 Comp.	M-1	1.40	C-1/C-2	1.30	
	2-4 Inv.	M-4	1.40	C-1/C-2	1.30	
2	2-5 Inv.	M-4	1.40	XXXI-15	1.30	
2	2-7 Inv.	M-3	1.40	C-1/C-2	1.30	
0 2	!-9 Inv.	M-3	1.40	XXXI-18	1.30	
·· 2	!-10 Inv.	M-3	1.40	XXXI-4/C-2	1.30	
2	2-14 Inv.	M-3	1.40	XXXI-4	1.30	
2	2-15 Inv.	M-3	1.40	XXXI-4	1.30	
2	-16 Inv.	M-3	1.35	XXXI-4	1.30	
2	2-18 Inv.	M-3	1.35	XXXI-4/C-2	1.25	
55 -	-19 Inv.	M-3	1.35	XXXI-4/C-3	1.30	

In the table, the gelatin amounts are shown in terms of  $g/m^2$ 

The resulting samples were each exposed to light through an wedge in the same manner as in Example-6 and processed in the following processing steps. Then, the same evaluations as made in Example-6 and the color developability evaluation were also made.

Processing step	Temperature	Time	
Color developing	$35.0 \pm 0.3^{\circ} C.$	45 sec.	

Add water to make in total of Adjust pH with sulfuric acid or potassium hydroxide to be

liter pH = 7.0

# Color developability

The maximum density, Dmax, of each sample resulted was measured with a densitometer, Model PDA-65 manufactured by Konica Corporation.

The results thereof are shown in Table-12.

				TARL	E 12	· · · · · · · · · · · · · · · · · · ·		·	
Sample No.	Color developability, Dmax			Photoptic color fading property, %		Dark color fading property, %			Color reproduction
	Magenta	Cyan	Yellow	Magenta	Cyan	Yellow	Magenta	Cyan	Synthetic evaluation of B, G, R
2- 1 Comp.	2.36	2.55	80	80	82	87	80	73	×
2- 4 Inv.	2.40	2.56	80	<b>4</b> 8	82	87	88	71	Δ
2- 5 Inv.	2.40	2.51	80	48	83	87	88	85	0
2- 7 Inv.	2.35	2.56	80	56	81	87	87	73	Δ
2- 9 Inv.	2.35	2.53	80	56	81	87	87	84	O.
2-10 Inv.	2.35	2.46	80	56	81	87	87	90	0
2-14 Inv.	2.33	2.47	80	80	83	87	88	86	0
2-15 Inv.	2.33	2.53	80	80	82	87	88	86	0
2-16 Inv.	2.36	2.56	80	79	82	87	88	86	0
2-10 Inv. 2-18 Inv.	2.36	2.54	80	79	80	87	88	- 89	0
2-19 Inv.	2.36	2.52	80	79	80	87	88	90	0

 $35.0 \pm 0.5^{\circ} C.$ 45 sec. Bleach-fixing 30 to 34° C. 90 sec. Stabilizing 60 sec. 60 to 80° C. Drying Developer 800 ml . Pure water 10 g Triethanolamine N.N-diethylhydroxylamine 0.02 g Potassium bromide Potassium chloride 0.3 gPotassium sulfite 1.0 g 1-hydroxyethylidene-1-1-diphosphoric acid 1.0 g Ethylenediaminetetraacetic acid 1.0 g Disodium catechol-3,5-disulfonic acid 4.5 g N-ethyl-N-\beta-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfonate 1.0 g Fluorescent whitening agent, 4,4'diaminostilbenedisulfonic acid derivative 27 g Potassium carbonate 1 liter Add water to make in total of pH = 10.10Adjust pH to be Bleach-fixer **6**0 g Ferric ammonium ethylenediaminetetraacetate dihydrate

3 g Ethylenediaminetetraacetic acid 100 ml Ammonium thiosulfate, in an aqueous 70% solution 27.5 ml Ammonium sulfite, in an aqueous 40% solution 1 liter Add water to make in total of pH = 5.7Adjust pH with potassium carbonate or glacial acetic acid to be Stabilizer 1.0 g 5-chloro-2-methyl-4-isothiazoline-3-one 1.0 g Ethylene glycol 2.0 g 1-hydroxyethylidene-1,1-diphosphoric acid 1.0 g Ethylenediaminetetraacetic acid 3.0 g Ammonium hydroxide, in an aqueous 20% solution 3.0 g Ammonium sulfite 1.5 g Fluorescent whitening agent, 4,4'diaminostilbenedisulfonic acid derivative

From the results shown in Table-12, it was proved that the combination of the couplers in Sample 2-1 was deteriorated in tones, and that the tones obtained from Samples 2-4 and 2-7 were found to be considerably improved by changing the couplers.

In the combinations of the couplers in the other samples than the above, they were excellent in color reproducibility and they had almost no color contamination 45 even through the visual observation.

In the combinations of the couplers and gelatin each used in Samples 2-15, 2-16, 2-18 and 2-19, the image preservability and color developability thereof were by no means inferior to others and the excellent characteristics including both of the three-color fading balance and color developability could be obtained. The abovementioned results were surprising and unexpected.

# Example-8

A mixture of 60 g of magenta coupler M-1, 15 g of dye-image stabilizer ST-4, 40 g of dye-image stabilizer ST-8 and 1.7 g of antistaining agent HQ-1 was dissolved in a mixture of 40 ml of high boiling organic solvent DBP and 100 ml of ethyl acetate. The solution resulted was added into an aqueous 5% gelatin solution containing 5 g of sodium dodecylbenzenesulfonate and the mixture thereof was then dispersed together by making use of a homogenizer. The resulting dispersed solution was made to be 1500 ml.

The resulting dispersed solution was added into 1000 65 ml of an aqueous 3% gelatin coating solution and, further, 400 g of a green-sensitive silver chlorobromide emulsion containing silver chloride of 80 mol % was added thereinto, so that a green-sensitive emulsion coating solution was prepared. In the same manner as in the

15

above, each of the other layer coating solutions was prepared. The resulting layer coating solutions were coated on a polyethylene-laminated paper support, in order from the support, so as to have the layer arrangements shown in Table-13.

TABLE 13

Layer	Composition	Amount added g/m ²
Layer 7	Gelatin	1.0
Protective layer		
Layer 6	Gelatin	0.6
UV absorbing	UV absorbent UV-1	0.2
layer	UV absorbent UV-2	0.2
•	Antistaining agent HQ-1	0.01
	DBP	0.2
	PVP	0.03
	Antiirradiation dye Al-2	0.02
Layer 5	Gelatin	1.40
Red-sensitive	Red-sensitive silver chloro-	0.24
layer	bromide emulsion, in terms of	
	silver content	
	Cyan coupler C-1	0.17
	Cyan coupler C-2	0.25
	Dye-image stabilizer ST-1	0.20
	Antistaining agent HQ-1	0.01
	DBP	0.30
Layer 4	Gelatin	1.30
UV absorbing	UV absorbent UV-1	0.40
layer	UV absorbent UV-2	0.40
-	Antistaining agent HQ-1	0.03
	DBP	0.40
Layer 3	Gelatin	1.40
Green-sensitive	Green-sensitive silver chloro-	0.27
layer	bromide emulsion, in terms of	
	silver content	
	Magenta coupler M-1	0.35
	Dye-image stabilizer ST-4	0.10
	Dye-image stabilizer ST-8	0.20
	DBP	0.30
. <u>.</u>	Antiirradiation dye AI-1	0.01
Layer 2	Gelatin	1.20
interlayer	Antistaining agent HQ-1	0.12
•	DBP	0.15
Layer I	Gelatin	1.30
Blue-sensitive	Blue-sensitive silver chloro-	0.30
ауег	bromide emulsion in terms of silver content	
	Yellow coupler Y-1	0.80
	Dye-image stabilizer ST-1	0.30
	Dye-image stabilizer ST-2	0.20
	Antistaining agent HQ-1	0.02
Summort	DBP Polyethylene-laminated paper	0.20
Support	Polyethylene-laminated paper	

$$OC_3H_{11}$$
 $OC_3H_{11}$ 
 $OC_3H_{12}$ 

As for the hardener, the foregoing H-1 was used.

The resulting sample was named Sample 1. Next, 55 Samples 2 through 12 were prepared in the same manner as in Sample 1, except that the yellow, cyan and magenta couplers and the total amount of gelatin added, each of Samples 1, were changed as shown in Table 14.

In addition, when changing the magenta coupler into the couplers of the invention, the following compounds were used together as the dye 7-image stabilizers.

$$O_2S$$
 $N$ 
 $OC_6H_{13}$ 
 $O.15 \text{ g/m}^2$ 
 $O.15 \text{ g/m}^2$ 
 $OC_6H_{13}$ 
 $O.15 \text{ g/m}^2$ 
 $OC_6H_{13}$ 
 $OC_6H_$ 

The resulting samples were exposed to light in an ordinary method and were then processed in the following processing steps.

•	Processing step	Temperature	Time
_	Color developing	33° C.	3 min. 30 sec.
<b>.</b> .	Bleach-fixing	33° C.	1 min. 30 sec.
25 _	Washing	33° C.	3 min.
	Color developer		
	N-ethyl-N-β-methanesulfo	<del>-</del>	4.9 g
	3-methyl-4-aminoaniline si		
	Hydroxylamine sulfate		2.0 g
30	Potassium carbonate	25.0 g	
	Sodium bromide	0.6 g	
	Sodium sulfite anhydride		2.0 g
	Benzyl alcohol		13.0 ml
35	Polyethylene glycol, having polymerization degree of	<del>-</del>	3.0 ml
	Add water to make	400	1 liter
	Adjust pH with sodium hy Bleach-fixer	ydroxide to be	pH = 10.0
	Ferric sodium ethylenedia	minetetraacetate	60.0 g
	Sodium thiosulfate		100.0 g
	Sodium bisulfite		10.0 g
0	Sodium metabisulfite		3.0 g
rU	Add water to make		1 liter
	Adjust pH with aqueous a	mmonia to be	pH = 7.0

The color reproducibility of each sample resulted was evaluated in the following manner.

# Color reproducibility

The color reproducibility evaluation was made according to the expression method of the Lauxvactoria color specification system specified in JIS Z-8729-1980, in the following manner. A u'v' chromaticity diagram was made out in terms of L = 50, and the synthetic color reproduction areas formed by the yellow, magenta and cyan color forming dyes were evaluated in terms of the area relative to that of Sample 1 which was regarded as a value of 100. In addition to the above evaluations, each of the color evaluations was visually made.

The results thereof are shown in Table-14.

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TABLE 14

			111000	A T		
	Yellow	Magenta	Cyan	Total amount of		Color duciblity
Sample No.	coupler in Layer 1	coupler in Layer 3	coupler in Layer 5	gelatin added, g/m ²	Relative area	Visual evaluation*
1 Comp.	Y-1	M-1	C-1/C-2	8.2	100	С
2 Comp.	Y-1	M-1	C-1/C-2	7.6	100	C
3 Comp.	XI-3	I-22	XXXI-4	8.2	119	B
4 Inv.	XI-3	<b>I-22</b>	XXXI-4	7.6	124	A
5 Inv.	XI-3	M-1	XXXI-4	7.6	125	Α
6 Inv.	X1-3	I-10	XXXI-4	7.6	124	Α
7 Inv.	XI-3	I-23	XXXI-4	7.6	127	Α

TABLE 14-continued

	Yellow	Magenta	Cyan	Total amount of		Color duciblity
Sample No.	coupler in Layer 1	coupler in Layer 3	coupler in Layer 5	gelatin added. g/m²	Relative area	Visual evaluation*
8 Inv.	X1-3	1-62	XXXI-4	7.6	125	Α
9 Inv.	XI-10	I-23	XXXI-4	7.6	126	Α
10 Inv.	XI-18	1-23	XXXI-4	7.6	125	Α
11 Inv.	X1-3	I-23	XXXI-8	7.6	126	Α
12 Inv.	XI-3	I-23	XXXI-15	7.6	124	Α

^{*}Evaluation levels

A: Hue and chroma were excellent

B: Hue was practically good, but chroma was seemed to be deteriorated with stains.

As can be understood from Table-14, in Samples 1 and 2 applied thereinto with the comparative couplers, their color reproduction were seriously deteriorated and almost no improvement effect was found out of the samples. Among the combinations of the couplers of the invention, in Samples 3 applied thereinto with gelatin in a total amount out of the range of the invention, each of the colors was still not clearly produced, because the chroma was deteriorated, though the hues were almost good; and in Samples 4 through 12, both of the hues and chroma were excellent and each of the colors was found 25 to be clear even in the visual judgements.

# Example 9

A sample was prepared by coating each of the layers each having the same compositions as in Sample 1 of 30 Example 8; provided, the silver halide emulsions used therein were prepared in the following manner. The resulting sample was named Sample 14.

Preparation of blue-sensitive silver halide emulsion

Into 1000 ml of an aqueous 2% gelatin solution being kept at 40° C., the following solutions A and B were simultaneously added with keeping their pAg values to be 6.5 and pH values to be 3.0 by taking 30 minutes and, thereinto the following solutions C and D were further 40 simultaneously added with keeping their pAg values to be 7.3 and pH values to be 5.5 by taking 180 minutes.

In this instance, each of the pAg control was made in accordance with the method described in Japanese Patent O.P.I. Publication No. 59-45437/1984, and each of 45 the pH control was made with an aqueous solution of sulfuric acid or sodium hydroxide.

·	· · · · · · · · · · · · · · · · · · ·	
3.42	g	د
0.03	g	
200	ml	
10	g	
200	ml	5
102.7	g	
	_	
600	ml	
300	g	6
600	ml	
	0.03 200 10 200 102.7 1.0 600	3.42 g 0.03 g 200 ml 10 g 200 ml 102.7 g 1.0 g 600 ml 300 g 600 ml

After completing the addition of the above-given solutions, the desalting treatment was made with an aqueous solution of 5% Demol N, manufactured by 65 Kao Corporation, and an aqueous solution of 2.0% magnesium sulfate. After then, the resulting desalted solution was mixed with an aqueous gelatin solution, so

that monodisperse type cubic emulsion EMP-1 was obtained. The average grain-size, variation coefficient and silver content thereof were 0.85  $\mu$ m, 0.07 and 99.5 mol %, respectively.

The resulting emulsion EMP-1 was chemically ripened at 50° C. for 90 minutes, with the following compounds, so that blue-sensitive silver halide emulsion EmA was obtained.

0.8 mg/mol AgX
0.5 mg/mol AgX
6 × 10 ⁻⁴ mols/mol AgX
$5 \times 10^{-4} \text{ mols/mol AgX}$

Preparation of green-sensitive silver halide emulsion

Monodisperse type cubic emulsion EMP-2 was obtained in the same manner as in EMP-1, except that the adding time of Solutions A and B and the adding time of Solutions C and D were changed. The average grain-size, variation coefficient and silver chloride content thereof were 0.43  $\mu$ m, 0.08 and 99.5 mol %, respectively.

EMP-2 was chemically ripened at 55° C. for 120 minutes with the following compounds, so that green-sensitive silver halide emulsion EmB was obtained.

Stabilizer SB-5 $6 \times 10^{-4}$ mols/mol AgX Sensitizing dye D-4 $4.0 \times 10^{-4}$ mols/mol AgX		Sodium thiosulfate Chloroauric acid	1.5 mg/mol AgX 1.0 mg/mol AgX
			$6 \times 10^{-4}  \text{mols/mol AgX}$
	0	Sensitizing dye D-4	$4.0 \times 10^{-4} \text{ mols/mol AgX}$

Preparation of red-sensitive silver halide emulsion

Monodisperse type cubic emulsion EMP-3 was obtained in the same manner as in EMP-1, except that the adding time of Solutions A and B and the adding time of Solution C an D were changed. The average grain-size, variation coefficient and silver chloride content thereof were 0.50 µm, 0.08 and 99.5 mol %, respectively.

EMP-3 was chemically ripened at 60° C. for 90 minutes with the following compounds, so that red-sensitive silver halide emulsion EmC was obtained.

1.8 mg/mol AgX
1.0 IIIE/ MOI VEN
2.0 mg/mol AgX
6 × 10 ⁻⁴ mols/mol AgX
0 × 10 ^{−4} mols/mol AgX

D-4

C: Hue and Chroma were deteriorated.

#### -continued

$$\begin{array}{c} O \\ C_2H_5 \\ O \\ CH=C-CH= \\ \\ (CH_2)_3SO_3\Theta \\ \\ (CH_2)_2SO_3H.N(C_2H_5)_3 \end{array}$$

Samples 15 through 24 were each prepared in the same manner as in Sample 14, except that the yellow, 20 magenta and cyan couplers and the total amount of gelatin added were replaced by those shown in Table-15.

Samples 14 through 24 were each exposed to light in an ordinary method and were then processed in the 25 following processing steps.

Processing step	Temperature	Time	
Color developing	35.0 ± 0.3° C.	45 sec.	
Bleach-fixing	$35.0 \pm 0.5^{\circ} C.$	45 sec.	
Stabilizing	30 to 34° C.	90 sec.	
Drying	60 to 80° C.	60 sec.	
Color developer			
Pure water		800 ml	
Triethanolamine		10 g	
N.N-diethylhydroxylan	nine	5 g	
Potassium bromide		0.02 g	
Potassium chloride		2 g	
Potassium sulfite		0.3 g	
1-hydroxyethylidene-1.	1-diphosphoric acid	1.0 g	
Ethylenediaminetetraacetic acid		1.0 g	
Disodium catechol-3.5-disulfonate		1.0 g	
N-ethyl-N-b-methanesulfonamidoethyl-		4.5 g	
3-methyl-4-aminoaniline	e sulfate		
Fluorescent whitening	agent. 4,4'-	1.0 g	
diaminostilbenedisulfon	ic acid derivative		
Potassium carbonate		27 g	
Add water to make in total of		1 liter	
Adjust pH to be		pH = 10.10	
Bleach-fixer			
Ferric ammonium ethylenediamine- tetraacetate dihydrate		60 g	
Ethylenediaminetetraacetic acid		3 g	
Ammonium thiosulfate, in an aqueous		100 ml	
70% solution			
Ammonium sulfite, in a	in aqueous 40%	27.5 ml	
solution			
Add water to make in	total of	1 liter	
Adjust pH with potassi	um carbonate	pH = 5.7	
or glacial acetic acid to	be be		

	•
-contin	nued

Stabilizer	
5-chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-hydroxyethylidene-1.1-diphosphoric acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide, in an aqueous	3.0 g
20% solution	
Fluorescent whitening agent. 4.4'-	1.5 g
diaminostilbenedisulfonic acid derivative	
Add water to make in total of	1 liter
Adjust pH with sulfuric acid or	pH = 7.0
potassium hydroxide to be	-

The color reproducibility of the processed samples were each evaluated in the same manner as in Example 8.

The processing time variation resistance of each samples were also evaluated in the following manner.

# Processing time variation resistance

The color developing time was changed from 45 seconds to 30 seconds. The ratios of the tone produced in the green-sensitive layer to each of the tones produced in the blue-sensitive and red-sensitive layers were obtained for both of the above-mentioned processing time and, then, the values of the ratios of the tones obtained by processing the samples in the 30-second process were so expressed as to be relative to the value, set at a value of 100, of the ratio of the tones obtained by processing the samples in the 45-second process.

In the manner, the tones were expressed by a value of the inclination 7 of the straight line between the densities, 0.80 and 1.80, obtained on the characteristic curve.

The results thereof are shown in Table-15.

the 45-second process

TABLE 15

Yellow coupler	Magenta coupler of Layer 3	Cyan coupler of Layer 5	Total amount of gelatin added, g/m ²	Color reproducibility		Processing time variation		
of Layer 1				Relative area	Visual judgement*	resistance		
						$\gamma B/\gamma G$	γ R/γ G	
Y-1	M-1	C-1/C-2	8.2	100	C	63	82	
Y-1	M-1	C-1/C-2	7.6	100	C	64	81	
<b>XI-3</b>	I-22	XXXI-4	8.2	118	В	72	70	
XI-3	I-22	XXXI-4	7.6	126	Α	88	89	
X1-3	M-1	XXXI-4	7.6	127	Α	88	89	
<b>XI-3</b>	I-10	XXXI-4	7.6	127	Α	89	91	
XI-3	1-23	XXXI-4	7.6	128	Α	92	92	
	coupler of Layer 1 Y-1 Y-1 XI-3 XI-3 XI-3 XI-3	of of Of Layer 1 Layer 3  Y-1 M-1 Y-1 M-1 XI-3 I-22 XI-3 I-22 XI-3 I-10	coupler         coupler         coupler           of         of         of           Layer 1         Layer 3         Layer 5           Y-1         M-1         C-1/C-2           Y-1         M-1         C-1/C-2           XI-3         I-22         XXXI-4           XI-3         I-22         XXXI-4           XI-3         M-1         XXXI-4           XI-3         I-10         XXXI-4	coupler         coupler         coupler         Total amount           of         of         of gelatin           Layer 1         Layer 3         Layer 5         added, g/m²           Y-1         M-1         C-1/C-2         8.2           Y-1         M-1         C-1/C-2         7.6           XI-3         I-22         XXXI-4         8.2           XI-3         I-22         XXXI-4         7.6           XI-3         M-1         XXXI-4         7.6           XI-3         I-10         XXXI-4         7.6	coupler         coupler         Coupler         Total amount         reproduct           of         of         of gelatin         Relative           Layer 1         Layer 3         Layer 5         added, g/m²         area           Y-1         M-1         C-1/C-2         8.2         100           Y-1         M-1         C-1/C-2         7.6         100           XI-3         I-22         XXXI-4         8.2         118           XI-3         I-22         XXXI-4         7.6         126           XI-3         M-1         XXXI-4         7.6         127           XI-3         I-10         XXXI-4         7.6         127           XI-3         I-10         XXXI-4         7.6         127	coupler         coupler         Coupler         Total amount         reproducibility           of         of         of gelatin         Relative         Visual           Layer 1         Layer 3         Layer 5         added, g/m²         area         judgement*           Y-1         M-1         C-1/C-2         8.2         100         C           Y-1         M-1         C-1/C-2         7.6         100         C           XI-3         I-22         XXXI-4         8.2         118         B           XI-3         I-22         XXXI-4         7.6         126         A           XI-3         M-1         XXXI-4         7.6         127         A           XI-3         I-10         XXXI-4         7.6         127         A	coupler         coupler         Total amount         reproducibility         time v           of         of         of gelatin         Relative         Visual         resist           Layer 1         Layer 3         Layer 5         added, g/m²         area         judgement*         γ B/γ G           Y-1         M-1         C-1/C-2         8.2         100         C         63           Y-1         M-1         C-1/C-2         7.6         100         C         64           XI-3         I-22         XXXI-4         8.2         118         B         72           XI-3         I-22         XXXI-4         7.6         126         A         88           XI-3         M-1         XXXI-4         7.6         127         A         88           XI-3         I-10         XXXI-4         7.6         127         A         89	

TABLE 15-continued

Sample No.	Yellow coupler of Layer 1	Magenta coupler of Layer 3	Cyan coupler of Layer 5	Total amount of gelatin added, g/m ²	Color reproducibility		Processing time variation	
					Relative area	Visual judgement*	resistance	
							γ Β/γ G	γ R/γ G
21 Inv.	XI-3	I-62	XXXI-4	7.6	126	Α	90	90
22 Inv.	<b>XI-</b> 10	I-23	XXXI-4	7.6	125	Α	88	91
23 Inv.	XI-3	I-23	XXXI-8	7.6	126	Α	90	90
24 Inv.	XI-3	I-23	XXX1-15	7.6	126	Α	90	89

- *Evaluation level
- A: Hue and chroma were excellent.
- B: Hue was nearly in fidelity, but chroma was deteriorated.
- C: Hue and chroma were both deteriorated.

As can be understood from Table-15, In Samples 14 and 15, the processing time variation resistance thereof were deteriorated as much as that the resistance were out of the permitted limit and any improvement effect could not be found out in the color reproducibility.

In Sample 16, the color reproducibility was improved by the combination of the couplers of the invention, however, the improvement thereof was still not satisfactory and, in addition, the processing time variation resistance was seriously deteriorated.

On the other hand, in Samples 17 through 24 in which the total amounts of gelatin added therein were reduced to be not more than the amount specified in the invention, the color reproducibility and processing time variation resistance were both improved and the effects of 35 the invention could be remarkably displayed in the rapid processing system using the high silver chloridecontaining emulsion.

Further, when applying a super-rapid process comprising a 20-second color developing step, a 20-second 40 bleach-fixing step and a 20-second stabilizing step to Samples 17 through 24 each of the invention, the effects of the invention could be obtained.

What is claimed is:

1. A silver halide photographic light-sensitive material comprising a support having thereon a photographic silver halide emulsion layer containing a magenta coupler, a photographic silver halide emulsion layer containing a yellow coupler, a photographic silver halide emulsion layer containing a cyan coupler and a non-light-sensitive layer containing a binder and a UV absorbent, wherein said silver halide photographic light-sensitive material has not more than 7.6 g/m² of gelatin, said UV absorbent is a compound represented by Formula a and has a melting point of from —100° to 55 15° C., and said magenta coupler is a compound represented by Formula I; with

$$R_3$$
 $R_1$ 
Formula a
 $R_1$ 
 $R_2$ 
 $R_3$ 
 $R_4$ 
 $R_5$ 
 $R_6$ 

wherein R₁, R₂, and R₃ each represent a hydrogen atom, an alkyl group or an alkoxy group, and

wherein Z represents a non-metallic group necessary to form a nitrogen-containing heterocyclic ring, X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent, and R represents a hydrogen atom or substituent.

2. The material of claim 1, wherein said magenta coupler is selected from the group consisting of compounds represented by the following Formulae II, III, IV, V, VI, and VII;

wherein X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent, and R₁, R₂, R₃, R₄, R₅,

R₆, R₇, and R₈ each represent a hydrogen atom or a substituent.

3. The material of claim 1, wherein said magenta coupler is a compound represented by the following Formula VII;

wherein  $Z_1$  represents a non-metallic group necessary to form a nitrogen-containing heterocyclic ring, X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent, and  $R_1$  represents a hydrogen atom or a substituent.

4. The material of claim 1, wherein R in said Formula 20 I is represented by the following Formula IX;

wherein R₉, R₁₀ and R₁₁ each represent a hydrogen atom or a substituent, at least two of R₉, R₁₀ and R₁₁ are combined to form a saturated or unsaturated ring, or all 30 of R₉, R₁₀ and R₁₁ are combined to form a cross-linking hydrocarbon compound.

5. The material of claim 1, wherein a substituent at Z in said Formula I is represented by the following Formula X;

wherein R¹represents an alkylene group and R² represents an alkyl group, a cycloalkyl group or an aryl 40 group.

6. The material of claim 2, wherein R₂through R₈ in said Formulae II through VI is represented by the following Formula X;

$$-R^1-SO_2-R^2$$
 Formula X

wherein R¹ represents an alkylene group and R² represents an alkyl group, a cycloalkyl group or an aryl group.

7. The material of claim 3, wherein a substituent of Z₁ in said Formula VII is represented by the following Formula X;

wherein R¹ represents an alkylene group and R² represents an alkyl group, a cycloalkyl group or an aryl group.

- 8. The material of claim 1, wherein said magenta 60 coupler is contained in an amount of  $1 \times 10^{-3}$  to 1 mol per mol of silver halide.
- 9. The material of claim 1, wherein said magenta coupler is contained in an amount of  $1 \times 10^{-2}$  to  $8 \times 10^{-1}$  mol per mol of silver halide.
- 10. The material of claim 1, wherein said non-light-sensitive photographic layer further contains a UV absorbent which is a compound represented b the fol-

lowing Formula a and solid at an ordinary temperature,

$$R_3$$
 $R_1$ 
 $R_2$ 
Formula a

wherein R₁, R₂ and R₃ each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alk-oxy group, an aryloxy group, an alkenyl group, a nitro group or a hydroxy group.

11. The material of claim 1, wherein said UV absorbent is contained in a proportion within the range of 0.1 to 300 % by weight based on the binder of the layer containing the UV absorbent.

12. The material of claim 1, wherein said UV absorbent is contained in a proportion within the range of 1 to 200 % by weight based on the binder of the layer containing the UV absorbent.

13. The material of claim 1, wherein said UV absor-25 bent is contained in a proportion within the range of 5 to 100 % by weight based on the binder of the layer containing the UV absorbent.

14. The material of claim 1, wherein said silver halide photographic light-sensitive material has 5.0 to 7.6 g/m² of gelatin.

15. The material of claim 1, wherein the material comprises silver halide grains having not less than 90 mol % of silver chloride, not more than 10 mol % of silver bromide, and not more than 0.5 mol % of silver iodide in the silver halide emulsion layer.

16. The material of claim 15, wherein the amount of the silver halide grains comprising not less than 90 mol % of silver chloride is not less than 60 % by weight based on the total amount of silver halide grains in the silver halide emulsion layer containing the silver halide grains comprising not less than 90 mol % of silver chloride.

17. The material of claim 15, wherein the amount of the silver halide grains comprising not less than 90 mol % of silver chloride is not less than 80 % by weight based on the total amount of silver halide 9rains in the silver halide emulsion layer containing the silver halide grains comprising not less than 90 mol % of silver chloride.

18. The material of claim 1, wherein said yellow coupler is a compound represented by the following Formula XI;

wherein R₁ represents an alkyl group, a cycloalkyl group or an aryl group, R₂ represents an alkyl group, a cycloalkyl group, an acyl group or an aryl group, R₃ represents a substituent, n is 0 or 1, R₄ represents a group having a carbonyl group or a sulfonyl group, J represents —N(R₅)CO— (wherein R₅ represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic ring), and X represents a group capable of being

split upon reaction with an oxidation product of a color developing agent.

19. The material of claim 1, wherein said cyan coupler is a compound represented by the following Formula XXXI;

wherein  $R^1$  represents an alkyl group having 2 to 6 of a carbon number,  $R^2$  represents a ballast group, and  $Z_1^{20}$  represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent.

20. The material of claim 1, wherein said cyan coupler is a compound represented by the following Formula XXXI;

Formula XXXI

wherein R¹ represents an alkyl group having 2 to 6 of a carbon number, R² represents a ballast group, and Z₁ represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent., and said magenta coupler is a compound represented by the following Formula XXXII;

$$R_2$$
 $R_3$ 
 $N$ 
 $N$ 
 $Z_2$ 
 $Z_2$ 

wherein R₁, R₂ and R₃ each represent a substituent, provided that they are the same as or different from each other, Z₂ represents an atomic group necessary to form a heterocyclic ring, and X represents a hydrogen atom or a group capable of being split upon reaction with an oxidation product of a color developing agent.

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# UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

5,112,728 PATENT NO. :

Page 1 of 2

DATED

May 12, 1992

INVENTOR(S): Masaki Tanji et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

# Title Page:

Item [30]: Priority Data, change "1-211738" to --1-261738--.

Item [30]: Priority Data, insert as additional Priority Data

-- Oct. 14, 1989 [JP] Japan.....1-267189-- and

-- Oct. 17, 1989 [JP] Japan.....1-269840--.

Claim 3, column 103, line 5, change "VII" to --VIII--.

Claim 7, column 103, line 51, after "substituent" change "of" to --at--.

claim 7, column 103, line 52, change "VII" to --VIII--.

claim 10, column 103, line 68, change "b" to --by--.

# UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO. :

5,112,728

Page 2 of 2

DATED

May 12, 1992

INVENTOR(S):

Masaki Tanji et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Calim 17, column 104, line 46, change "9rains" to --grains--.

Signed and Sealed this

Twentieth Day of September, 1994

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks